FINAL REPORT

Evaluation of Potential for Monitored Natural Attenuation of Perchlorate in Groundwater (Indian Head)

ESTCP Project ER-200428

JULY 2010

Tony M. Lieberman **Solutions IES, Inc.**

Sheri L. Knox Solutions IES, Inc.

Robert C. Borden **Solutions IES, Inc.**

This document has been cleared for public release



including suggestions for reducing	completing and reviewing the collect this burden, to Washington Headqu uld be aware that notwithstanding ar DMB control number.	arters Services, Directorate for Infor	mation Operations and Reports	, 1215 Jefferson Davis I	Highway, Suite 1204, Arlington		
1. REPORT DATE JUL 2010	3. DATES COVERED						
4. TITLE AND SUBTITLE				5a. CONTRACT	NUMBER		
	ntial for Monitored ndian Head) ESTCI			5b. GRANT NUMBER			
in Groundwater (1	nuian Heau) ESTCI	Froject EK-200426		5c. PROGRAM E	5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)				5d. PROJECT NU	MBER		
				5e. TASK NUMBER			
				5f. WORK UNIT	NUMBER		
	ZATION NAME(S) AND AC curity Technology C cense	` '	a U.S.	8. PERFORMING REPORT NUMB	ORGANIZATION ER		
9. SPONSORING/MONITO	RING AGENCY NAME(S) A	ND ADDRESS(ES)		10. SPONSOR/M	ONITOR'S ACRONYM(S)		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAIL Approved for publ	LABILITY STATEMENT ic release, distributi	on unlimited					
13. SUPPLEMENTARY NO The original docum	otes nent contains color i	mages.					
14. ABSTRACT							
15. SUBJECT TERMS							
16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF				18. NUMBER	19a. NAME OF		
a. REPORT unclassified	SAN		OF PAGES 159	RESPONSIBLE PERSON			

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and

Report Documentation Page

Form Approved OMB No. 0704-0188

Table of Contents

1.0 Introduction	1
1.1 Background	1
1.2 Objectives of the Demonstration	2
1.3 Regulatory Drivers	
1.4 Stakeholder/End-User Issues	
2.0 Technology Description	
2.1 Monitored Natural Attenuation (MNA) Development	
2.2 Advantages and Limitations of the Technology	
2.2.1 Cleanup Objectives	
2.2.2 Advantages of MNA	
2.2.3 Limitations of MNA	
3.0 Demonstration Design and Evaluation	
3.1 Performance Objectives for the Demonstration	
3.2.2 Previous Remediation Studies	
3.2.2.2 Enhanced Perchlorate Biodegradation	
3.2.3 Pre-Demonstration Testing	
3.2.3.1 Groundwater and Soil Sampling	13
3.2.3.2 Laboratory Microcosm Studies	14
3.2.4 Selection Criteria for Building 1419 Site, NSWC, Indian Head	
3.3 Demonstration Approach	17
3.4 Field Methods	
3.4.1 Determination of Geomorphologic Zones	
3.4.2 Boring and Monitoring Well Installation	
3.4.2.1 Zone 1 - Land Borings and Monitor Wells	
 3.4.2.2 Zone 2 – Littoral Zone Monitor Wells and Piezometers 3.4.2.3 Zone 3 – Subtidal Channel and Surface Water Monitoring Points 	
3.4.2.4 Zone 4 - Monitoring Well Installation in the Subtidal Shallows	
3.4.3 Groundwater and Creek Sediment Pore Water Sampling	
3.4.4 Measurement of Hydraulic Head in Wells and Piezometers	
3.4.5 Determination of Aquifer Hydraulic Conductivity	
3.5 Laboratory Methods	
3.5.1 Sampling for Standard Analyses	
3.5.2 Groundwater Collection for Perchlorate Analysis	
3.5.3 Biological Assays –qPCR Analysis	
3.6 <i>In Situ</i> Biodegradation Testing	
3.6.1 <i>In Situ</i> Columns	
3.6.2 Macrocosms	
3.6.3 Stable Isotope Analysis	
3.7 Residuals Handling	
4.0 Site Area Hydrogeology	
4.1 Regional Hydrogeology	
4.1 Regional Hydrogeology 4.2 Local Subsurface Conditions	
4.2.1 Subsurface Conditions in the Site Area.	
4.2.1 Subsurface Conditions in the Site Area	
4.2.2 Hydraune Conductivity of the Surficial Adulter	
4.3.1 Groundwater Flow in Zone 1 - Mainland.	
T.7.1 SIQUIUWALU I IVW III ZOUU I = WAHHAHU	++

4.3.2	Groundwater Flow in Zones 2 and 3 – Littoral Zone and Subtidal Channel	45
4.3.3	Groundwater Flow in Zone 4 - Subtidal Shallows	47
4.3.4	Groundwater Discharge Rates	
4.4	Geochemical Indicators of Groundwater Flow Patterns	
4.4.1	Temperature	
4.4.2		
	Generalized Hydrogeologic Model	
5.0 Co	nceptual Model of Perchlorate Transport and Fate	54
	eld MNA Evaluation Program	
6.1	Tier 1 Evaluation – Plume Geometry and Stability	
6.1.1	Plume Geometry	59
6.1.2	Plume Stability	
6.1.3	Effect of Dilution on Perchlorate Concentrations	
6.1.4	Source Area Attenuation	
6.1.5	Mass Flux	
6.1.6	Summary of Plume Geometry and Stability Evaluation (Tier 1)	
	Tier 2 Evaluation – Biogeochemical Parameters and Biological Indicators	
6.2.1	Total (or Dissolved) Organic Carbon	
6.2.2	Oxidation-Reduction Potential	
6.2.3	Dissolved Oxygen	
6.2.4	Nitrate	
6.2.5	Iron	
6.2.6	Methane	
6.2.7	pH	
6.2.8	Temperature	
6.2.9	Chloride, Chlorate and Chlorite	
	Microbial Populations	
6.2.11	, ,	
	Tier 3 Evaluation – Biodegradation Rates	
6.3.1	Macrocosm Study	
6.3.2	· · · · · · · · · · · · · · · · · · ·	
	rformance Assessment	
	Primary Performance Objectives.	
	Secondary Performance Objectives	
	st Assessment	
	Cost Drivers	
	Indian Head Demonstration Costs and Long-term Cost Model	
	Cost Comparison: MNA vs. Passive <i>In Situ</i> and Active Pumping Technologies	
8.3.1	Basis of Cost Comparison	
	plementation Issues	
	Environmental Checklist	
	Other Regulatory Issues	
	End-User Issues	
10.0	Deferences	104

Figures

- 1-1 Perchlorate Biodegradation Pathway
- 3-1 Aerial View of Indian Head NSWC
- 3-2 Demonstration Area Showing NSWC Vicinity and the Indian Head Project Site
- 3-3 Site Map with Building Locations
- 3-4 Shaw Test Plot and Select Monitoring Well Locations
- 3-5 Microscosm Bottles Used in the Laboratory Studies
- 3-6 Biodegradation of Perchlorate in Laboratory Microcosms
- 3-7 Aerial View of the Demonstration Area
- 3-8 Open Grassy Area Southeast of Drum Storage Building
- 3-9 Wooded Area Looking Northeast from Mattawoman Creek
- 3-10 Creek Bank and High Tide Line
- 3-11 Vegetation Covering the Littoral Zone during the Summer Months
- 3-12 Littoral Zone without Vegetation during the Winter Months
- 3-13 Organic Muck in the Littoral Zone
- 3-14 Subtidal Channel
- 3-15 Physiographic Zones in the Demonstration Area
- 3-16 Monitor Well and Piezometer Network
- 3-17 Piezometer Installation in the Littoral Zone using a Slide Hammer
- 3-18 *In Situ* Column Locations in the Littoral Zone
- 3-19 In Situ Columns IC-3 and IC-4 adjacent to Piezometer Group 1
- 3-20 In Situ Column Construction
- 3-21 Preparing Macrocosms in 5-Gallon Carboys
- 4-1 Generalized Stratigraphic and Hydrologic Framework of the Indian Head Area
- 4-2 Section A-A'
- 4-3 Section B-B'
- 4-4 Section C-C'
- 4-5 Water Table Contour Map (April 2008)
- 4-6 Variation in Water Elevations from Oct. 24 to Nov. 1, 2006 in Piezometer Group SGP-23 Installed in the Subtidal Channel
- 4-7 Measured Hydraulic Gradients between Different Depths in Piezometer Groups 1 and 2 on Three Dates
- 4-8 Temperature Fluctuations in Surface, Shallow and Deep Groundwater
- 4-9 Chloride Concentrations in March 2007 at Different Sampling Locations
- 4-10 Vertical Profiles of Choride Concentration vs. Depth in Littoral Zone (Piezometer Groups 1 and 2) and Subtidal Channel (SGP-23 and SGP-24).
- 4-11 Flow Net for Study Area
- 5-1 Presumed Source and Conceptual Discharge Areas
- 5-2 Conceptual Model of Perchlorate Transport
- 5-3 Photograph Showing Organic Muck Layer

- 6-1 Perchlorate Concentration Map (April 2008)
- 6-2 Geochemical Changes in Shallow and Deep Groundwater and Sediment Pore Water
- 6-3 Perchlorate (ClO₄) and Chloride (Cl) Concentration vs. Depth in Piezometer Groups 1 and 2
- 6-4 Perchlorate Concentration vs. Time Curve Fit for MW-4
- 6-5 Mass Flux Evaluation Area
- 6-6 Orientation of Mass Flux Transects
- 6-7 Changes in Total Organic Carbon along Transects B-B' and C-C'
- 6-8 Oxidation-Reduction (Redox) Potential for Degradation Processes
- 6-9 Changes in Oxidation-Reduction (ORP) Potential along Transects B-B' and C-C'
- 6-10 Map of pH Concentrations in Deep Groundwater/Pore Water beneath the Site
- 6-11 Perchlorate Concentration and pcrA Gene Copies in Monitor Wells in August 2008
- 6-12 Relationship between Perchlorate Concnetration and *pcrA* Gene Copies
- 6-13 Relationships between Number of *pcrA* Gene Copies, ORP, and pH in Monitor Wells in August 2008
- 6-14 Nitrate, Perchlorate, and Electron Acceptor Concentration vs. Time in Five Replicate Macrocosms Constructed with Littoral Zone Sediment
- 6-15 Regression Analysis of Nitrate, Perchlorate and Electron Acceptor Concentration vs. Time
- 6-16 Locations of *In Situ* Columns
- 6-17 Comparison of Macrocosm and In Situ Column Rates

Tables

3-1	Performance	Ob.	iectives

- 3-2 Groundwater Chemistry and Perchlorate Concentrations in Monitor Wells
- 3-3 Performance Monitoring Schedule
- 3-4 Sample Collection and Analysis Details
- 4-1 Aquifer Test Results
- 4-2 Average and Range of Horizontal Hydraulic Conductivity in Zones 1 to 4
- 6-1a Perchlorate Concentrations (µg/L) in Littoral Zone Points
- 6-1b Perchlorate Concentrations (µg/L) in Littoral Zone Piezometer Groups
- 6-1c Perchlorate Concentrations (µg/L) in Subtidal Channel Monitoring Points
- 6-2 Groundwater and Surface Water Mixing Rations in Piezometer Groups 1 and 2
- 6-3 First-Order Concentration vs. Time Attenuation Rates in Zone 1 Wells
- 6-4a Groundwater Flux Calculations
- 6-4b Perchlorate Mass Flux Calculations
- 6-5 Performance Monitoring in Shallow Wells
- 6-6 Performance Monitoring in Deep Wells
- 6-7 Comparison of DO, Iron, and Methane Levels in SGP-22D, -23D and -24D
- 6-8 Dissolved Iron Concentrations in Shallow and Deep Groundwater
- 6-9 Seasonal Groundwater Temperature Comparison
- 6-10 Nitrate, Perchlorate, and Electron Acceptor Degradation Rates in Littoral Zone Macrocosms
- 6-11 Analytical Results of Groundwater Samples Collected from *In Situ* Columns during Pumping
- 6-12 Biodegradation Rates Calculated from *In Situ* Biodegradation Study at IC-1
- 6-13 Summary of Perchlorate Concentrations at Equivalent Time
- 6-14 Summary of First-Order Biodegradation Rates
- 8-1 Actual and Estimated Future Costs for Implementation of Perchlorate MNA for the Indian Head Site
- 8-2 Summary of Site Characteristics and Design Parameters for Biological Treatment of Perchlorate-Impacted Groundwater
- 8-3 Cost Components for Passive Injection Biobarrier Treatment of Perchlorate-Impacted Groundwater
- 8-4 Cost Components for Extraction and Treatment of Perchlorate-Impacted Groundwater
- 8-5 Cost Components for Perchlorate MNA
- 8-6 Summary of Capital Costs and NPV of Costs for Operation and Monitoring for Biological Treatment of Perchlorate-Impacted Groundwater

Appendices

Appendix A	Monitoring Well/Piezometer Construction Details & Select Boring Logs
Appendix B	Historical Water Level Measurements
Appendix C	Performance Monitoring Data
Appendix D	Natural Attenuation Rate Calculations
Appendix E	Mass Flux Calculations
Appendix F	Macrocosm Study Results
Appendix G	Points of Contact

List of Abbreviations and Acronyms

AFCEE Air Force Center for Engineering and the Environment

AP Ammonium Perchlorate

BOD Biochemical Oxygen Demand

CD Chlorite Dismutase Enzyme *cld* Chlorite Dismutase Gene

CVOCs Chlorinated Volatile Organic Compounds
CSIA Compound Specific Isotope Analysis

DO Dissolved Oxygen
DoD Department of Defense

DPRB Dissimilatory Perchlorate-Reducing Bacteria

ESTCP Environmental Security Technology Certification Program

ft bgs Feet Below Ground Surface

IC In Situ Column

IDW Investigation-Derived Waste

K Hydraulic Conductivity Constant

MDE Maryland Department of the Environment

MNA Monitored Natural Attenuation MBT Molecular Biology Tool mRNA Messenger Ribonucleic Acid

NCSU North Carolina State University NSWC Naval Surface Warfare Center

NPV Net Present Value

O&M Operation and Maintenance ORP Oxidation-Reduction Potential

PCE Tetrachloroethene (Tetrachloroethylene)

pcrA Perchlorate Reductase Gene A

PI Principal Investigator
PID Photoionization Detector
PPE Personal Protective Equipment

PV Pore Volume PVC Polyvinyl Chloride

qPCR Quantitative Polymerase Chain Reaction Analysis

RAO Remedial Action Objective

sq. ft. Square FeetSW Surface Water

SWMU Solid Waste Management Unit

TBC To Be Considered Regulatory Standard

TCE Trichloroethene
TOC Total Organic Carbon

USEPA United States Environmental Protection Agency

USGS United States Geologic Service

VOA Volatile Organic Analysis VOC Volatile Organic Compound

Acknowledgements

Solutions-IES gratefully acknowledges the financial and technical support provided by ESTCP. We appreciate the guidance provided by Dr. Andrea Leeson (ESTCP Environmental Restoration Program Manager), Erica Becvar (Contracting Officer's Representative), and the ESTCP reviewers. Solutions-IES team members contributing to this project include:

Dr. Robert C. Borden, P.E. (Principal Investigator), M. Tony Lieberman (co-Principal Investigator), Sheri L. Knox, P.E (Project Manager) with support by Walt Beckwith, P.G., Jessica L. Keener, P.G., Sean Jarvah, Dawn Marshall, and Brian Rebar. Laboratory analysis and macrocosm studies by David Black and Aaron Weispfenning at North Carolina State University are also appreciated as well as the molecular biology analyses provided by Microbial Insights, Inc. and Dr. Kate Scow at University of California - Davis. Solutions-IES extends thanks to Carey Yates, Sean Jorgensen and Mark Yeaton at Indian Head Naval Surface Warfare Center for their cooperation and assistance and who facilitated site access and the field work discussed in this report.

Executive Summary

Introduction

Solutions-IES conducted a demonstration of the potential for Monitored Natural Attenuation (MNA) to be used as a groundwater remedy for perchlorate at a site located on the Naval Surface Warfare Center near Indian Head, MD. The work was funded by the Environmental Security and Technology Certification Program (ESTCP Project ER-0428). The overall objectives of this project were to provide Department of Defense (DoD) managers with the tools needed to: (1) identify sites where MNA may be appropriate for management of perchlorate releases; and (2) demonstrate to regulatory agencies that perchlorate MNA can be effective for controlling adverse impacts to the environment. The project used a tiered approach described by Solutions-IES in a Protocol also prepared as part of this project. The Protocol, titled "Natural Attenuation of Perchlorate in Groundwater: Processes, Tools, and Monitoring Techniques" (ESTCP, 2008), guides the end user through the process of developing multiple lines of evidence to support perchlorate MNA.

After a detailed site-selection process, the Indian Head project site was chosen for the demonstration. The Indian Head site consists of approximately 2 acres of grassy land bounded on the east and south by Mattawoman Creek, a large, tidally influenced tributary of the Potomac River. Two buildings are on the site: Building 1419 and a small drum storage building. Building 1419 was once used to clean out or "hog-out" solid propellant containing ammonium perchlorate from various devices, including rockets and ejection seat motors that had exceeded their useful life span. The hog-out process and former waste handling methods impacted the groundwater with elevated concentrations of perchlorate. The groundwater flow direction suggested that perchlorate-contaminated groundwater migrates approximately 460 ft until reaching Mattawoman Creek,

Demonstration

At the onset of the evaluation a small monitoring well network was already in place. This network had been installed to monitor the source of perchlorate contamination and evaluate a pilot test of enhanced *in situ* bioremediation in 2002 by Shaw Environmental near Building 1419. The prior work indicated that perchlorate concentrations decreased with distance away from the presumed source at Building 1419. However, perchlorate was not monitored beyond the pilot test area, which was located midway between the presumed source area and Mattawoman Creek, where the perchlorate plume was expected to discharge.

In 2005, Solutions-IES commenced its evaluation of the potential for MNA at the site. After baseline monitoring was performed, it became apparent that additional monitoring well/peizometer installations would be required to fully assess the plume geometry including areas closer to the creek. Additional monitoring wells and piezometers were installed in four geomorphologic areas of the site: a) on land downgradient of the source area and closer to the creek; b) in the Littoral Zone, c) in the Subtidal Shallows, and d) in the Subtidal Channel located between the Littoral Zone and Subtidal Shallows.

Originally, perchlorate concentrations as high as $93,000 \,\mu\text{g/L}$ were measured in groundwater near Building 1419; concentrations 460 ft downgradient beneath the bank of the creek remain over $10,000 \,\mu\text{g/L}$. The Site Conceptual Model suggested that the changes in perchlorate concentration in groundwater beneath the land were controlled mostly by groundwater flow, dilution and dispersion, with a limited biological component. The model also hypothesized that the majority of the 99% decrease in perchlorate concentration occurred as groundwater migrates upward through the organic rich sediments in the Littoral Zone near the creek, with biodegradation as a significant mechanism for removal in this zone. The tiered approach presented in the Protocol was used to develop lines of evidence to support the Site Conceptual Model and evaluate MNA as a groundwater remedy for perchlorate at this site.

Tier 1 – Perchlorate Plume Geometry and Stability.

The well network was used to define current perchlorate conditions across the site. Where available, historical data were used to supplement current findings to examine attenuation of perchlorate. Monitoring results show the perchlorate plume is generally stable and there is no evidence of continuing downgradient migration. Within the Littoral Zone, perchlorate concentrations decline much more rapidly than would be expected based on dilution alone indicating biodegradation within the organic rich sediments is the dominant attenuation mechanism. Mass flux calculations indicate that over 99.9% of the perchlorate mass is degraded during migration through the organic rich sediments of the shallow Littoral Zone. In several source area monitor wells, perchlorate concentrations are gradually declining with time. If current trends continue, perchlorate concentrations in these wells will drop below the "To Be Considered" value of $24.5 \,\mu\text{g/L}$ established by the USEPA within 30 years.

Tier 2- Biogeochemical Parameters and Biological Indicators

As part of the *Tier 2* evaluation, bio-geochemical parameters and biological indicators were monitored in wells throughout the perchlorate plume. Monitoring results indicated that biogeochemical conditions in many of the land wells were not conducive to perchlorate biodegradation including: (a) low TOC levels; (b) positive ORP values, and (c) elevated nitrate concentrations. In contrast, biogeochemical conditions in the shallow Littoral Zone wells are excellent for perchlorate biodegradation: (a) TOC is above 2 mg/L; (b) ORP drop below +50 mV; (c) nitrate declines below the analytical detection limit; (d) dissolved iron and methane are elevated; and (e) very high numbers of perchlorate degrading bacteria are present in the zone where perchlorate concentrations decline rapidly.

Tier 3-Biodegradation Indicators

Additional laboratory and field tests were employed to provide direct evidence of perchlorate biodegradation and estimate biodegradation rates. Macrocosm incubations were set up using soil from the Littoral Zone and groundwater from a nearby well. Macrocosms showed at least a 40% reduction in perchlorate in less than 10 days which is equivalent to a 1st-order biodegradation rate of 0.12 per day.

In situ columns were installed within the Littoral Zone to provide a direct measure of bioactivity. The columns were constructed to isolate a column of soil from the surrounding soil and water. Groundwater was slowly pumped upward through each open-ended column to induce a controlled flow through the organic rich zone. Perchlorate concentrations at the bottom and top of the column during pumping were compared and 1st-order biodegradation rates were estimated ranging from 0.12 to 0.63 per day.

Biodegradation rates in the macrocosms and *in situ* columns were consistent with observed rates of perchlorate disappearance in monitor wells installed within the littoral zone, suggesting these approaches may be useful for estimating field scale attenuation rates.

Summary

Data on groundwater flow, plume configuration, site-specific biogeochemical conditions, microbial populations and perchlorate attenuation by both abiotic and biological processes provided multiple lines of evidence that perchlorate is naturally attenuating at the Indian Head site prior to discharge to Mattawoman Creek. The Tier 1, 2 and 3 evaluations demonstrated that MNA was effective in meeting all primary and secondary performance objectives established in the demonstration plan. Biogeochemical conditions in the shallow Littoral Zone wells are excellent for perchlorate biodegradation, resulting in greater than 99.9% decline in mass flux prior to discharge. Perchlorate concentrations were reduced below the USEPA primary remediation goal prior to discharge to Mattawoman Creek. When conditions are appropriate, a MNA evaluation is relatively simple to implement and reliable, with few scale up constraints. The MNA process does not generate significant process wastes. The estimated life-cycle cost for implementation of MNA is estimated to be approximately one half the cost of a Passive Injection Biobarrier and one third the cost of Extraction and Treatment.

The project met the objectives by identifying, evaluating, and utilizing lines of evidence as a tool to evaluate perchlorate MNA as a remedial strategy for the Indian Site. These lines of evidence, now established, can be used to demonstrate perchlorate MNA is effective for controlling adverse impacts to the environment at the Indian Head Site and support acceptance of MNA as the groundwater remedy.

Lessons Learned

➤ In this demonstration project, Tier 1, 2 and 3 evaluations were performed to demonstrate perchlorate attenuation. However at typical sites, a Tier 3 evaluation may not always be required and Tier 1 and 2 evaluations may be sufficient to demonstration perchlorate MNA.

- Monitoring data collected during this study suggest that field measurements of dissolved oxygen did not provide a reliable indicator of *in situ* redox conditions and the potential for perchlorate reduction.
- In this project, perchlorate was reduced to below detectable levels in every sample with greater than $10^2 \, pcr A$ copies/mL (> $10^5 \, pcr A/L$). The absence of detectable perchlorate when there is > $100 \, pcr A/mL$ constitutes strong evidence for effective natural attenuation due to biodegradation. Monitoring for this gene is a useful indicator of perchlorate biodegradation.

1.0 Introduction

Monitored Natural Attenuation (MNA) is a potential alternative for management of large diffuse perchlorate plumes in a cost-effective manner. Natural attenuation is defined by the USEPA as the "biodegradation, diffusion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility or volume to levels that are protective of human health and the environment" (USEPA, 1997). The term MNA refers to the reliance on natural attenuation processes, within the context of a carefully controlled and monitored site cleanup, to achieve site-specific remedial goals.

Perchlorate is an important contaminant of concern, particularly to the Department of Defense (DoD) as a result of historical use, release and/or disposal of solid rocket fuel and munitions containing ammonium perchlorate. To evaluate whether natural attenuation of perchlorate occurs in the field, lines of evidence need to be established and validated. As part of this project funded by the Environmental Security Technology Certification Program (ESTCP Project No. ER-0428), two sites were selected for field demonstrations to evaluate the potential for perchlorate MNA as a groundwater remedy: 1) near Building 1419 at the Naval Surface Warfare Center (NSWC), Indian Head, Maryland (Indian Head site) and 2) a TCE/Perchlorate Solid Waste Management Unit (SWMU) at an industrial facility in Elkton, Maryland. The two overall goals of this project were:

- 1. Document the extent of perchlorate natural attenuation in the field and the effectiveness in controlling adverse impacts to the environment; and
- 2. Provide DoD managers with the tools needed to evaluate whether MNA may be appropriate for management of perchlorate–impacted groundwater on their site(s).

MNA of perchlorate in groundwater was evaluated using a tiered approach described in the technical Protocol developed by Solutions-IES, Inc. in 2008 (ESTCP, 2008). The tiers include: 1) plume stability and geometry assessment; 2) biogeochemical parameter and biological indicator evaluation; and 3) biodegradation rate estimation. This technical report documents the evaluation of MNA of perchlorate contamination in groundwater at the Indian Head site. Documentation of perchlorate MNA at the Elkton, MD site is presented in a separate report.

1.1 Background

Releases of perchlorate have resulted in extensive contamination of surface and groundwater supplies. Perchlorate is a highly mobile, soluble anion that sorbs poorly to most aquifer material. There are a wide variety of microorganisms can degrade perchlorate to chloride and oxygen under oxygen limiting conditions (Coates et al., 1999; Coates and Pollock, 2003; Coates and Jackson, 2009). Perchlorate-reducing organisms are widespread in the environment (Coates et al., 1999; Logan, 2001; Coates and Jackson, 2009) and can use a variety of different organic substrates (e.g., acetate, propionate, lactate, etc.) as electron donors for perchlorate reduction (Herman and Frankenberger, 1998; Coates et al., 1999). Perchlorate biodegradation can occur under anoxic and strongly reducing anaerobic conditions. In addition, some facultative perchlorate reducers are capable of both aerobic respiration under low oxygen tension and anaerobic respiration when oxygen is not present. This metabolic versatility suggests that

perchlorate reducing microorganisms will be active in a variety of environments, increasing the potential for perchlorate MNA.

Oxygen is an inhibitor of perchlorate reduction, but the absence of oxygen alone is not enough to induce the perchlorate-reducing enzymes to function. Facultative anaerobic perchlorate metabolism is inhibited by dissolved oxygen (DO) concentrations in excess of 2 mg/L (Rikken et al., 1996; Chaudhuri et al., 2002). Nitrate can also negatively affect the activity of perchlorate reductase enzymes. However, when sufficient biodegradable organic substrate is present, the available DO and nitrate will be rapidly consumed and perchlorate will biodegrade (Coates and Jackson, 2009). Trace amounts of molybdenum are also required due to its functional role in the biochemistry of the perchlorate reductase enzyme (Chaudhuri et al., 2002). The biodegradation pathway of perchlorate is illustrated below (**Figure 1-1**).

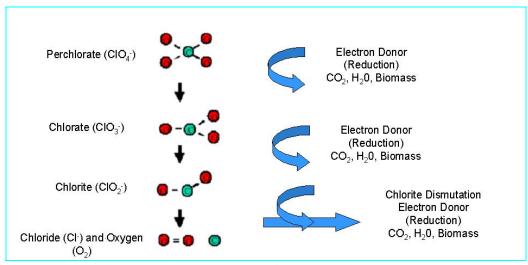


Figure 1-1. Perchlorate Biodegradation Pathway

Work by Coates et al. (1999), Chaudhuri et al. (2002), and Bender et al. (2002) indicates that the <u>Dechloromonas</u> and <u>Azospira</u> groups represent the primary chlorate and dissimilatory perchlorate reducing bacteria (DPRB) in the environment, but more that 30 different strains of perchlorate-reducing microbes have been identified (USEPA, 2005). The rate-limiting step in the three-step degradation process is the conversion of perchlorate to chlorate by a perchlorate reductase enzyme (Coates and Jackson, 2009). Subsequent conversion of chlorate to chlorite is also catalyzed by a perchlorate reductase enzyme. Chlorite removal by the chlorite dismutase (CD) enzyme is the final step in perchlorate reduction.

Where applicable, MNA is will often be the least costly groundwater remediation technology. However, practitioners should first document the rate and extent of perchlorate attenuation in the field through multiple lines of evidence.

1.2 Objectives of the Demonstration

A list of potential demonstration sites was generated through a questionnaire sent to knowledgeable representatives at approximately 120 potential DoD or DoD-related sites nationwide. By comparing the responses received to the selection criteria in the Technology Demonstration Plan, these were pared down to seven potential sites for further study. Samples

were then collected from each of these sites and microcosm studies were then performed to measure attenuation of perchlorate in a laboratory setting. The details of the site selection process and results of microcosm testing were documented in a prior report titled "Field and Laboratory Evaluation of the Potential for Monitored Natural Attenuation of Perchlorate in Groundwater, Final Technical Report" (i.e., Treatability Report; ESTCP, 2007). Based on the microcosm studies, site logistics, and cost considerations, two sites in Maryland were selected to evaluate the potential for MNA of perchlorate in groundwater. This report describes the field demonstration at the Indian Head site. The objectives of the technical demonstrations were to:

- Further develop and evaluate lines of evidence established during the site selection process for their applicability to MNA.
- Evaluate the use of microbiological indicators of perchlorate degradation.
- > Compare biodegradation rates measured in microcosm studies with biodegradation rates in the field.
- Evaluate the cost-effectiveness of MNA of perchlorate at the Indian Head site.
- Transfer the knowledge gained about perchlorate MNA to the regulatory community.

1.3 Regulatory Drivers

The discharge of perchlorate to the environment can impact ground and surface water with the potential for human consumption through direct (drinking water) and indirect (crop uptake from irrigation water) pathways. Sampling performed by the USEPA in 2004 revealed that over 11 million people in the United States had greater than 4 μ g/L in their drinking water (Stroo et al., 2009). It appears that the primary exposure to perchlorate in the United States is through consumption of food (USFDA, 2007). This is a concern because high levels of perchlorate interfere with iodide uptake by the thyroid (NRC, 2005)

Through 2005, a federal cleanup standard for perchlorate in groundwater or soil had not been promulgated (USEPA, 2005; ITRC, 2005). However, in January 2006, the USEPA issued "Assessment Guidance for Perchlorate" identifying 24.5 μ g/L as the "to be considered" (TBC) value and preliminary remediation goal for perchlorate (USEPA, 2006). Since then several states have identified advisory levels that range in concentration from 1 μ g/L to 18 μ g/L (Hatzinger, 2005). Massachusetts promulgated the first state drinking water standard for perchlorate in 2006, at 2 μ g/L (MADEP, 2006) and California has established a drinking water standard of 6 μ g/L (CDHS, 2007). During the course of this project, Maryland adopted a perchlorate standard of 2.6 μ g/L in drinking water (MDE, 2008).

1.4 Stakeholder/End-User Issues

An overall goal of this project was to develop a protocol that could be used to evaluate MNA of perchlorate as a remedial strategy. The technical demonstrations at the Indian Head and Elkton, MD sites were used to evaluate the procedures described in the Protocol "Natural Attenuation of Perchlorate in Groundwater: Processes, Tools and Monitoring Techniques" (ESTCP, 2008). Where MNA is protective of human health and the environmental, it is often the least costly alternative in the short term. However, the process is not fast and the longer project life cycles can sometimes result in greater long-term costs. MNA should not a "no action" approach to groundwater treatment.

In the past, MNA has not been commonly applied for management of perchlorate plumes, in part, because there was no guidance for implementing this technology. The Protocol developed from this study (ESTCP, 2008) helps direct end-users select the correct tools for evaluating use of MNA of perchlorate as a remedial alternative for their particular site. By properly applying the steps described in the Protocol, local regulators and the general public can gain confidence that MNA of perchlorate is protective of the public welfare, human health and the environment.

2.0 Technology Description

2.1 Monitored Natural Attenuation (MNA) Development

In the 1980s and 1990s, field monitoring data indicated that many groundwater plumes were not migrating as far as predicted, and in some cases, were stable or receding. Detailed laboratory and field research demonstrated that the combined action of naturally occurring physical, chemical, and biological processes was limiting downgradient migration and adverse impacts, without any active human intervention. As a result of this work, Monitored Natural Attenuation (MNA) became a widely accepted practice for effective management of groundwater contamination. MNA is the use of these natural processes, along with careful documentation and monitoring, to manage contaminated sites.

The USEPA and others have developed protocols and guidance documents for implementing MNA for specific contaminants. Published methods for evaluating MNA of petroleum hydrocarbons (Wiedemeier et al, 1995; USEPA, 1999) and chlorinated solvents (USEPA, 1998) have been in use for many years. These documents describe systematic steps for delineating contaminant plumes, describing trends in contaminant fate and transport, monitoring site geochemistry, testing site biology and even scoring the site for its potential to support natural attenuation (USEPA, 1998). Wiedemeier et al. (1998) developed a tiered approach to systematize the process of documenting MNA at any given site. The three tiers are as follows:

- ➤ Tier 1 Plume Stability and Geometry Assessment
- ➤ Tier 2 Biogeochemical Parameter and Biological Indicator Evaluation
- ➤ Tier 3 Biodegradation Rate Estimation

Prior to current work, MNA of perchlorate had not been systematically tested in the field. One objective of this demonstration was to identify useful indicators of perchlorate attenuation that would be applicable to field sites. The information gained during this project was also used to demonstrate a technical Protocol for implementing this technology at perchlorate contaminated sites (ESTCP, 2008).

2.2 Advantages and Limitations of the Technology

2.2.1 Cleanup Objectives

The objective of all remediation approaches should be to return groundwater to its beneficial uses within a timeframe that is reasonable given the particular circumstances of the site. MNA is an appropriate remediation method when its use is protective of human health and the environment and it is capable of achieving site-specific remediation objectives within a timeframe that is reasonable compared to other alternatives. Over the short-term, the contaminant plume should be stable or shrinking. Over the long-term, the mass and/or concentration of contaminants should decrease.

2.2.2 Advantages of MNA

Natural attenuation includes a range of physical, chemical and biological processes. Because perchlorate is an inorganic salt, it is very soluble and mobile in groundwater. High solubility is both an advantage and disadvantage. Flushing and dilution can reduce concentrations rapidly,

but solubility can result in extended plumes with low concentrations that are difficult to capture and expensive to treat.

As paraphrased from the Wiedemeier et al. (1998), primary advantages of using MNA as a technology for remediating perchlorate in groundwater are:

- ➤ Lower volume of remediation derived wastes ;
- Reduced potential for cross-media transfer of contaminants;
- ➤ Reduced risk of human exposure to contaminants, contaminated media and other hazards:
- Some natural attenuation processes result in *in situ* destruction of contaminants;
- Less disturbance to site operations and ecological receptors;
- ➤ No artificial impact to groundwater geochemistry and biology;
- > Can be applied to all or a portion of a site depending on site characteristics and goals;
- > Can easily be used in combination with other technologies; and
- ➤ Lower capital costs and low, if any, maintenance costs.

2.2.3 Limitations of MNA

The primary limitations of MNA include:

- ➤ Potential longer life cycles to reach remediation goals compared to active remediation measures;
- ➤ More detailed site characterization is needed to demonstrate attenuation which may result in more complex and costly up-front investigation;
- ➤ Institutional controls may be required to ensure long-term protectiveness;
- ➤ Long-term performance monitoring will often be more expensive and for a longer time period;
- > Potential exists for continued contaminant migration, and/or cross-media transfer of contaminants:
- > Changing site conditions over time may require a re-evaluation of MNA; and
- ➤ Public acceptance may be more difficult and costly to obtain.

3.0 Demonstration Design and Evaluation

3.1 Performance Objectives for the Demonstration

The overall objective of this project was to evaluate the potential for monitored natural attenuation of perchlorate in groundwater. Once perchlorate attenuation is demonstrated, regulators and site owners can evaluate use of MNA along with other remediation strategies. If natural attenuation processes are not sufficient to prevent significant adverse impacts, other remediation strategies may need to be implemented before application of MNA.

Qualitative and quantitative performance objectives were developed in the Technology Demonstration Plan (Solutions-IES, 2006) to demonstrate the MNA of perchlorate in groundwater. As shown in **Table 3-1**, all the performance objectives were achieved. Sections of the report where each objective is discussed are noted in the table.

3.2 Site Selection Process

To identify sites for participation in the perchlorate MNA project, three levels of site screening were conducted. Screening Level 1 was performed in the office and involved gathering historical information from approximately 120 perchlorate-impacted sites across the United States. Past remediation activities, if any, were considered. Screening Level 2 included reviewing the gathered information and selecting seven sites for comparative field characterization. The seven sites selected for further screening included:

- 1. Little Mountain Test Annex Sludge Drying Beds, Hill AFB, Utah
- 2. ATK Thiokol, Inc., Utah
- 3. Beale Air Force Base, California
- 4. John C. Stennis Space Center, Mississippi
- 5. Redstone Arsenal, Alabama
- 6. Manufacturing Facility, Elkton, Maryland
- 7. Naval Surface Warfare Center, Indian Head, Maryland

Level 3 screening included collection and analysis of soil and groundwater samples from the seven field sites selected during the Level 2 screening step. The site matrices collected were analyzed in the laboratory for parameters potentially useful for determining the suitability of the site for MNA of perchlorate. These included field measurements such as pH, DO and oxidation-reduction potential (ORP), and laboratory analysis of perchlorate concentration, total organic carbon (TOC) concentration, CD enzyme analysis, and 6-month biological oxygen demand (BOD₆). Detailed information about the screening process and the results of the analyses performed at all seven sites is provided in the Treatability Report (ESTCP, 2007). Additional site-matrix sediments and groundwater were collected from perchlorate-impacted areas of each site to use in laboratory microcosm studies. The pre-demonstration findings associated with the selection of the Indian Head site are described in the following sections.

Table 3-1 Performance Objectives						
Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance (Objective Met?)	Detailed Discussion		
Qualitative	1. Reduce risk	Reduce concentrations and mass flux of perchlorate during downgradient migration	Yes	Section 6.1		
	2. Capital costs	Capital costs are significantly lower than active remedial alternatives.	Yes	Section 8.0		
	3. Maintenance	Maintenance costs are low and are typical of those associated with maintaining a monitoring well network.	Yes	Section 8.0		
	4. Uncomplicated implementation	Implementation is similar to that of a typical monitoring program.	Yes	Sections 3.3, 3.4, 3.5 and 6.0		
	5. Regulatory acceptance	MNA approach is generally accepted by regulatory community, with conditions.	Yes	Sections 1.3 and 2.1, 2.2 9.2		
	6. Monitoring approach	Monitoring approach is consistent with current industry practice. Results are easy to understand and interpret.	Yes	Sections 3.3, 3.4, 3.5 and 6.0		
Quantitative	1. Reduce perchlorate concentrations	> 90% reduction in average perchlorate concentration in wells downgradient of the probable source area.	Yes	Sections 6.1.1 and 6.1.2		
	2. Reduce mass flux of perchlorate	Reduce mass flux of perchlorate by >75% between source area and the most downgradient line of monitor wells.	Yes	Section 6.1 and 6.1.5		
	3. Multiple lines of evidence	Two or more lines of evidence support perchlorate attenuation.	Yes	Sections 6.1, 6.2 and 6.3		
	4. Enzyme activity	RNA levels of perchlorate degraders are elevated at some locations in the plume relative to background locations.	Yes	Section 6.2.10		
	5. Meet regulatory standards	Perchlorate concentrations are below regulatory levels at compliance point.	Yes	Sections 6.1 and 6.3		

3.2.1 Indian Head Site Description

The following discussion of the history and site conditions are from available literature and site documents made available during preliminary work at Indian Head in 2005. The *Field Demonstration of In Situ Perchlorate Bioremediation at Building 1419* (Cramer et al., 2004) was used as the primary source of historical information about the NSWC. Mr. Mark Yeaton of the

Indian Head Environmental Program Office provided additional history and became the site contact subsequent to Mr. Cramer's departure from the project in 2006.

The Town of Indian Head and the NSWC are located approximately 30 miles south of Washington, DC on a narrow peninsula (neck) of land bounded to the north by the Potomac River and to the south by Mattawoman Creek (**Figure 3-1**).



Figure 3-1. Aerial View of Indian Head NSWC (Image from U.S. Geological Survey, http://earthexplorer.usgs.gov/, modified 10/27/2007)

Both the Potomac River and Mattawoman Creek are tidal estuaries of the Chesapeake Bay estuary system. The surficial (water table) aquifer at the site consists of more recent saturated alluvial soil resting on top of the Patapsco clay that is encountered at approximately 16 feet below ground surface (ft bgs). The surficial aquifer is unconfined and varies in its position seasonally in response to precipitation and evapotranspiration. The water table surface generally slopes similarly to the land surface topography with the effect that upland areas generally serve as groundwater recharge areas and low areas generally serve as groundwater discharge areas.

Figure 3-2 shows portions of the Town of Indian Head and NSWC from the USGS Indian Head 7.5' Topographic Map. The demonstration area lies within the marked rectangle. This area of the NSWC including the Building 1419 site is shown in **Figure 3-3**.

The demonstration area consists of approximately 2 acres starting approximately 60 feet southeast of Building 1419 and extending to Mattawoman Creek. Building 1419 was used to clean out or "hog-out" solid propellant containing ammonium perchlorate from various devices, including rockets and ejection seat motors that have exceeded their useful life span. The hog-out process and former waste handling methods impacted the groundwater near Building 1419.

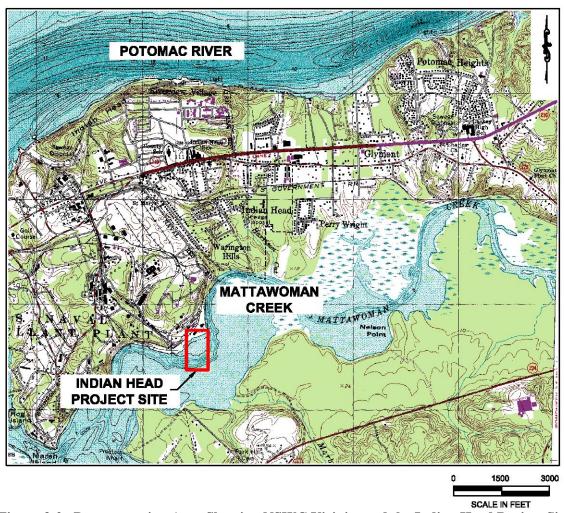


Figure 3-2. Demonstration Area Showing NSWC Vicinity and the Indian Head Project Site (Image from U.S. Geological Survey, 7.5 Minute Topographic Map, Indian Head, MD-VA, 1966, Photorevised 1978; Bathymetry added 1982)

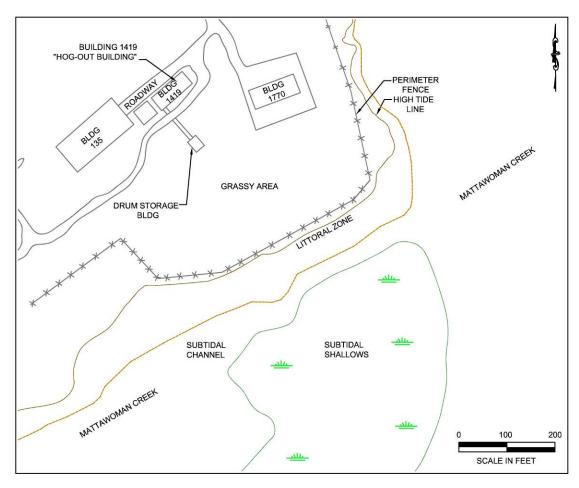


Figure 3-3. Site Map with Building Locations

3.2.2 Previous Remediation Studies

3.2.2.1 Source Identification

In 2001, ESTCP funded an independent study at this site to demonstrate and validate the use of passive flux meters for measuring groundwater and perchlorate fluxes (ESTCP, 2006). The study showed that perchlorate flux did not change over time from 2002 through 2005, indicating the presence of a persistent source of perchlorate near MW-1 since no perchlorate-contaminated hog-out wastewater had been discharged since 1996. Measurements of vertical perchlorate flux suggested the possibility of a vadose zone source that would continuously release perchlorate to the aquifer by recharge induced by rainfall. This phenomenon could be used to explain high temporal variability of perchlorate concentrations observed in MW-3 and MW-4, located 180 and 125 ft downgradient from the presumed source area near Building 1419, respectively (**Figure 3-4**).

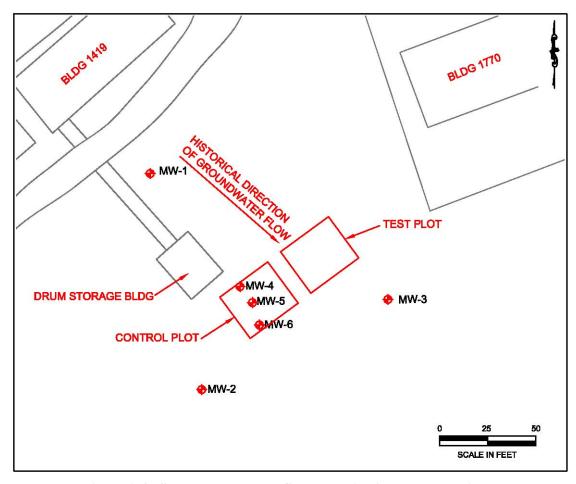


Figure 3-4. Shaw Test Plot and Select Monitoring Well Locations

3.2.2.2 Enhanced Perchlorate Biodegradation

In 2002, Shaw Environmental, Inc. (Shaw) investigated the Building 1419 site as part of a pilot study evaluating the use of enhanced *in situ* bioremediation (Cramer et al., 2004; Hoponick, 2006). A perchlorate plume was identified extending approximately from the rear of Building 1419 toward Mattawoman Creek. The limits of the plume were not delineated, but perchlorate concentrations ranging from 8 to 430 mg/L were reported along with pH ranging mostly between 4.2 and 5.6. The groundwater velocity was estimated to be between 0.4 and 1.4 ft/d based on slug test data which indicated an average hydraulic conductivity of 0.012 ft/min (ESTCP, 2006).

The study area used by Shaw for their pilot test is located southeast of Building 1419 and approximately 350 feet northwest of Mattawoman Creek. Shaw constructed a pilot system employing a recirculation cell design consisting of two 30 X 30-ft areas (**Figure 3-4**) approximately 9-ft apart. The surficial geology of the test area was described as consisting of 2 to 4 feet of fill including organic soils, gravel, and silty sand (Cramer et al., 2004). The underlying 11 to 13 feet consisted of mottled light to olive brown clay to sandy silts. The clay and sand fractions of the silts varied horizontally and vertically. Fine-grained sand seams 1 to 2 inches in thickness were seen in many of the boring locations, but the sand seams did not appear to be continuous across the site. A 1.0 to 1.5-ft thick layer of sand and gravel was encountered in the borings at a depth of approximately 15 to 16 ft bgs. The sand and gravel did appear to be

continuous beneath the study area. The sand and gravel was found to be underlain by gray clay, which extended to a depth of at least 20 ft bgs. The saturated thickness was found to be approximately 10 feet in the vicinity of the pilot test. The average hydraulic gradient was 0.023 ft/ft (ESTCP, 2006).

In the test cell, groundwater was extracted from the site, amended with sodium lactate substrate and a bicarbonate/sodium carbonate pH buffer, and then re-injected into the aquifer. Groundwater was extracted and re-injected without substrate or buffer amendment in the control area near MW-6. The study was conducted for 20 weeks. In the Control cell in which only water was circulated, there was no change in perchlorate concentration. In the Treatment cell amended with lactate and buffer, the results demonstrated that:

- ➤ "Naturally occurring perchlorate-degrading bacteria are present in the groundwater underlying (the Bldg 1419 site);
- > these organisms can be stimulated to degrade perchlorate from more that 50 mg/L to below detection using lactate as a food source; (and)
- ➤ the pH of the aquifer must be buffered to achieve optimal perchlorate biodegradation" (Cramer et al., 2004).

Lactate concentrations exceeded 100 mg/L in groundwater in most of the Treatment cell monitoring wells during the course of the recirculation. After 111 days, lactate addition was stopped and by 140 days, no lactate was detected in groundwater.

3.2.3 Pre-Demonstration Testing

3.2.3.1 Groundwater and Soil Sampling

In February 2005, Solutions-IES collected groundwater samples from three existing monitor wells (MW-1, MW-2 and MW-4) to evaluate the potential for long-term impacts from the prior in situ bioremediation pilot test. ORP, DO and pH were measured in the field and samples were also submitted to laboratory analysis of perchlorate, chlorinated volatile organic compounds (CVOCs), TOC, methane, ethane, ethene, nitrate, sulfate and chloride. MW-4 was located in the vicinity of the former lactate injection treatment cell. Solutions-IES also collected saturated soil samples using a hand auger immediately adjacent to MW-2 and MW-4. These samples were analyzed for CD enzyme activity and TOC. Semi-quantitative CD enzyme assays were performed by Microbial Insights, Inc. of Rockford, TN.

Table 3-2 shows the results of the evaluation and compares groundwater conditions in 2002 prior to implementing the Shaw pilot study and the samples collected three years later by Solutions-IES (ESTCP, 2007). Perchlorate concentrations measured in 2005 were noted to be lower than those reported in 2002 in MW-2 and MW-4. There was no change in MW-1 near the source, which is consistent with the mass flux findings reported in ESTCP (2006). CD enzyme assays of soil collected near MW-2 were strongly positive, while CD results on soil collected near MW-4 were more variable (+/-). Changes in MW-4 may be related to proximity to the Shaw Treatment cell in 2002. The near neutral pH in MW-2 likely supported increased biological activity resulting in reduced perchlorate concentrations in this well.

Table 3-2
Groundwater Chemistry and Perchlorate Concentrations in Monitor Wells

Well ID No.	Sample Date	Perchlorate (µg/L)	DO (ppm)	ORP (mV)	pH (SU)	TOC (mg/L)	Methane (μg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
	2/5/2002	84,700	1.5	NA	5.0	NA	NA	NA	NA	NA
MW-1	2/14/2005	92,820	~1.0	105	4.9	2.2	15.7	113	38.0	16.1
	2/5/2002	1,900	NR	NA	6.8	NA	NA	NA	NA	NA
MW-2	2/14/2005	3	~3.5	< -1000	6.9	4.4	BQL	2.3	64.2	1.4
	2/5/2002	181,000	1.6	NA	5.0	NA	NA	NA	NA	NA
MW-4	2/14/2005	36,263	~8	5.6	5.4	2.2	80.2	8.7	116	11.3

Data from February 5, 2002 from Cramer et al. (2004).

Data from February 14, 2005 from ESTCP (2007).

NA = Not analyzed; NR = No Reading.

There was little indication of residual organic carbon in groundwater in proximity of the Shaw Treatment cell and the sediment near MW-4 contained only 240 mg/kg TOC. By contrast, the sediment near MW-2, which was shown to have lower perchlorate and a more reducing environment, was reported to contain 3,500 mg/kg TOC. In general, perchlorate concentrations remain elevated across the site, indicating that the long-term impact from the lactate injection would not likely complicate a demonstration of perchlorate MNA at the Indian Head site.

3.2.3.2 Laboratory Microcosm Studies

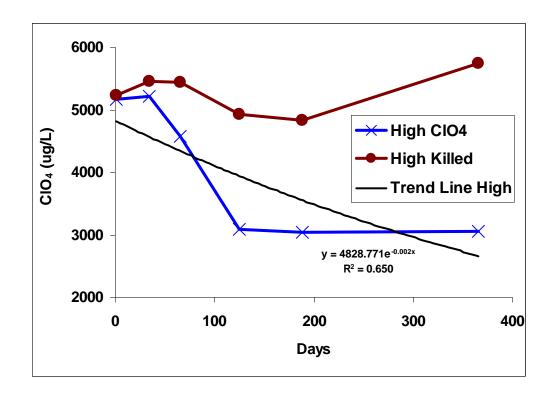
Cramer et al. (2004) reported no biodegradation activity in unamended controls in microcosms created from sediment and groundwater from the Building 1419 site. However, the incubation period was for only 71 days. Solutions-IES created 250-mL microcosm bottles using saturated soil from near MW-2 and groundwater from MW-2 to test three conditions: natural attenuation of perchlorate (ambient conditions) starting at relatively low concentrations (i.e., ~100 to 200 μ g/L); natural attenuation of perchlorate starting at relatively high concentrations (i.e., ~5,000 μ g/L); and, for comparison, enhanced attenuation in the presence of added simple and complex electron donors (i.e., lactate and EOS^{®1} solutions, respectively) (**Figure 3-5**). The treatments testing natural attenuation received no amendments unless perchlorate had to be added to achieve the desired starting concentration. Poison/killed controls were used to monitor for abiotic losses.

¹ EOS[®] is a registered trademark of EOS Remediation LLC, Raleigh, NC. The product, EOS[®] 598 B42, was provided by the manufacturer for use in this study.



Figure 3-5. Microcosm Bottles Used in the Laboratory Studies

The microcosms were incubated at room temperature and monitored for approximately one year. Samples were tested for the changes in concentration with time of perchlorate, methane, DO, nitrate, sulfate, and chloride, and perchlorate (ESTCP, 2007). The results of the microcosms starting with both high (spiked) and low (background) concentrations of perchlorate are shown in **Figure 3-6**. The results indicate that the concentrations of perchlorate declined slowly, but measurably, in unamended microcosms with both high and low starting concentrations. In the presence of an organic substrate (EOS®), the concentration of perchlorate quickly decreased below detection indicating that bacteria with perchlorate-reducing capacity were present in the environment and could be readily stimulated to achieve high rates of biodegradation. Compared with the substrate-enhanced treatment, the unamended, ambient high and low rates were much slower, with first-order biodegradation rates of only 0.002/d (1/yr) and 0.01/d (5/yr), respectively. In the killed control microcosms, the concentrations of perchlorate and other electron acceptors (nitrate and sulfate) remained constant over time substantiating the observed reduction in perchlorate in ambient microcosms was due to biological activity.



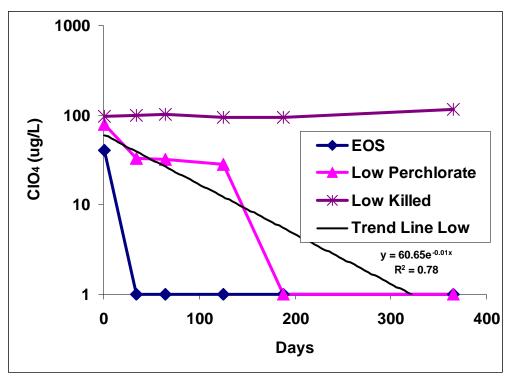


Figure 3-6. Biodegradation of Perchlorate in Laboratory Microcosms (Constructed using Sediment and Groundwater from MW-2) (Source: ESTCP, 2007)

3.2.4 Selection Criteria for Building 1419 Site, NSWC, Indian Head

Subsequent to the sampling activities and laboratory studies performed during Screening Level 3, a scoring system was devised to assist in the evaluation of the seven sites of interest for technical demonstration. In similar fashion to the preliminary screening analysis for evaluating the MNA of chlorinated volatile organic compounds (Wiedemeier et al., 1998), the parameters monitored in Screening Levels 2 and 3 were assigned scores based on the likelihood that each criterion would be conducive to natural attenuation and a successful technical demonstration.

The geochemical data from the Indian Head site that were factored into its selection were obtained from MW-2 and MW-4 as shown in **Table 3-2**. The field monitoring results from the Indian Head site suggest the presence of measurable dissolved oxygen in the groundwater, but the ORP measurements vary widely from strongly oxidative to very reducing. The groundwater pH generally was below optimal, but there were indications that some areas of the site could support biodegradation. Although TOC was low in groundwater, some TOC was reported in sediments and large declines in perchlorate were observed in MW-2 and MW-4 over a 3-year period.

The CD enzyme assay on sediments from the site, along with the positive results in the microcosm study conducted by Solutions-IES, and the pilot study performed by Shaw, support the presence of dissimilatory perchlorate reducing bacteria (DPRB) in the aquifer. In the low perchlorate ambient microcosms constructed with sediment and groundwater from MW-2, nitrate and perchlorate were depleted in all the three replicates suggesting potential for natural perchlorate biodegradation to occur.

Additional criteria were also factored into the evaluation included site logistics such as accessibility, weather, presence of unexploded ordnance and accessible terrain. The depth to groundwater and type of drilling required, which relates to cost, as well as the interest of the base managers in supporting the project were also considered. Based on this analysis, the Indian Head site was selected and approved by ESTCP as one of two demonstration sites.

3.3 Demonstration Approach

Widespread acceptance of MNA will require multiple lines of evidence to demonstrate its value as a remedial alternative. Analytical methods are available to monitor the concentration of perchlorate in the environment with high sensitivity and selectivity, geochemical tests can indicate whether ambient conditions are conducive to perchlorate biodegradation, and molecular biological tools are available to monitor the activity and sustainability of perchlorate-reducing bacterial populations. When properly applied, MNA of perchlorate and can be protective of human health and the environment.

The MNA Protocol created during the early stages of the project, was used as guidance in our evaluation of the potential for MNA of perchlorate at the Indian Head site. The objective was to use the three-tiered approach, adopted from the USEPA (1999) and described in the Protocol, to evaluate how this approach would work for perchlorate on a real project site. As noted in Section 2.1 above, the tiers include: 1) plume stability and geometry assessment, 2) biogeochemical parameter and biological indicator evaluation; and 3) biodegradation rate estimation.

With some minor exceptions, the tiers were followed to help guide the planning and selection of tasks to address the challenges at the site.

The demonstration activities included both field and laboratory components. Groundwater sampling activities were performed five times over the course of the performance monitoring period to evaluate aquifer conditions, and how those conditions might affect the potential for natural biodegradation of perchlorate. As described in Section 3.4.2, the well network was expanded during the course of the work. Therefore, not all wells were available or sampled during each event. The groundwater sampling events were conducted over a 3-year period (~38 months) on the dates shown in the **Table 3-3**.

Table 3-3 Performance Monitoring Schedule						
Sampling Date	Days	Months				
2/15/2005	0	0				
11/17/2005	275	~9				
9/28/2006	590	~19				
8/9/2007	905	~30				
4/17/2008	1,157	~38				

3.4 Field Methods

Field activities were adapted to evaluate the fate and transport of perchlorate through different surface conditions encountered as groundwater moves from the area near Building 1419 to Mattawoman Creek. Field methods implemented during the demonstration included the installation of borings, monitor wells and piezometers, instantaneous and continuous water level determinations, measurement of field parameters and hydraulic conductivity, and installation and testing of specialized *in situ* columns to measure perchlorate biodegradation rates. Because of the physical conditions at the site were variable, the following sections describe four different geomorphologic zones at the Indian Head site and serves as a precursor to understanding the groundwater flow conditions and perchlorate attenuation at the site.

3.4.1 Determination of Geomorphologic Zones

The remediation studies described in Cramer et al. (2004) and ESTCP (2006), as well as the predemonstration testing conducted by Solutions-IES (ESTCP, 2007) focused on the area between the presumed source of perchlorate outside Building 1419 and monitor wells and Geoprobe borings approximately 150 ft downgradient. It became evident early in the demonstration that the perchlorate plume was not entirely delineated and likely extended to near Mattawoman Creek. To assess the potential for perchlorate MNA, additional groundwater monitoring points would be needed along the flowpath to Mattawoman Creek and the assessment would have to take into account both surface and aquifer conditions within the land area south of Building 1419 and extending into Mattawoman Creek.

Figure 3-7 is an aerial view of the demonstration area which includes the following structures: Building 135, incinerator building (Building 1770), and Building 1419 with a sidewalk leading to the small drum storage building. Mattawoman Creek flows along the east side of the site before turning to the west. The creek bank is along the southern extent of the trees (darker

green) in the photograph. The lighter blue-green colored vegetation appearing in the creek consists of wetland plants growing in submerged alluvium that has been deposited on both sides of the creek channel.

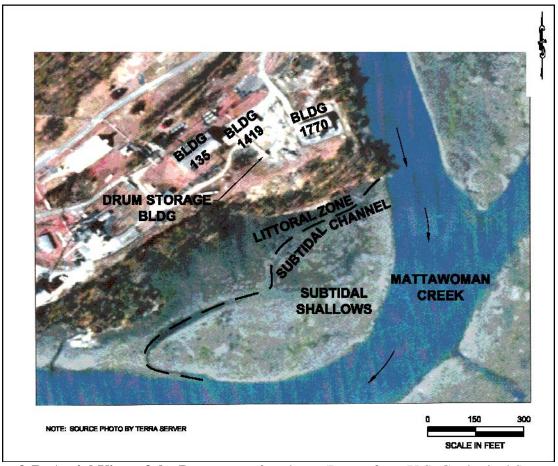


Figure 3-7. Aerial View of the Demonstration Area (Image from U.S. Geological Survey, Marbury, Maryland, USA, 3/17/1994; downloaded from http://msrmaps.com, 2009)

The Indian Head site can be subdivided into four different zones based on land use, geomorphology, physiography and vegetation. The land area south of Building 1419, also referred to as Zone 1, comprises approximately 2 acres from Building 1419 south to the high tide line on the north bank of Mattawoman Creek. The open area just south of Buildings 1419 and 1770 is covered in grass that is mowed periodically (**Figure 3-8**).



Figure 3-8. Open Grassy Area Southeast of Drum Storage Building (Remnants of Shaw Pilot Study remain on site.)



Figure 3-9. Wooded Area Looking Northeast from Mattawoman Creek



Figure 3-10. Creek Bank and High Tide Line

Further south, the area is covered with deciduous trees with some evidence (cross ties) of a previous railroad spur line (**Figure 3-9**). The spur was reportedly used to unload rail cars containing nitric and hydrochloric acid. The land surface slopes gently to the south. The facility is surrounded with a perimeter chain link fence that follows the creek bank. Outside the fence the land surface slopes downward 3 to 5 feet to the high tide line forming the creek bank (**Figure 3-10**).

Zones 2 through 4 are located within Mattawoman Creek. The Littoral Zone is defined as the region that is above the low-water mark and below the high-water mark, i.e., exposed to air at low tide and submerged at high tide. The Littoral Zone always includes the intertidal zone and is often used to mean the same as the intertidal zone.

The width of the Littoral Zone ranges between 50 and 100 feet wide (80 feet average). During the warmer months of the year, Zone 2 is covered in vegetation such as *Pontederia cordata* (pickerelweed) and *Zizaniopsis miliacea* (giant cut grass) and other wetland vegetative species (**Figure 3-11**).



Figure 3-11. Vegetation Covering the Littoral Zone during the Summer Months

In the winter, Zone 2 is generally devoid of vegetation (**Figure 3-12**). The surficial sediments within Zone 2 are highly organic muck silt and sand (**Figure 3-13**).



Figure 3-12. Littoral Zone without Vegetation during the Winter Months



Figure 3-13. Organic Muck in the Littoral Zone

The Subtidal Channel (Zone 3) is a relatively narrow channel-like depression that parallels the creek bank at the edge of the Littoral Zone. The channel is between 10 and 20 feet wide and is devoid of vegetation throughout the year (**Figure 3-14**).



Figure 3-14. Subtidal Channel

The Subtidal Shallows (Zone 4) is a 400- to 600-ft wide expanse of accreted sediment located south of the Subtidal Channel along an inside meander of Mattawoman Creek. Zone 4 is submerged with 6 to 18 inches of water at low tide and is defined by a covering of *Nelumbo lutea* (American lotus) which are visible beyond the Subtidal Channel in the photograph **Figure 3-14.** The main channel for Mattawoman Creek is located south and west of the Subtidal Shallows and is approximately 200 feet wide. **Figure 3-15** shows the relative position of the four physiographic zones.

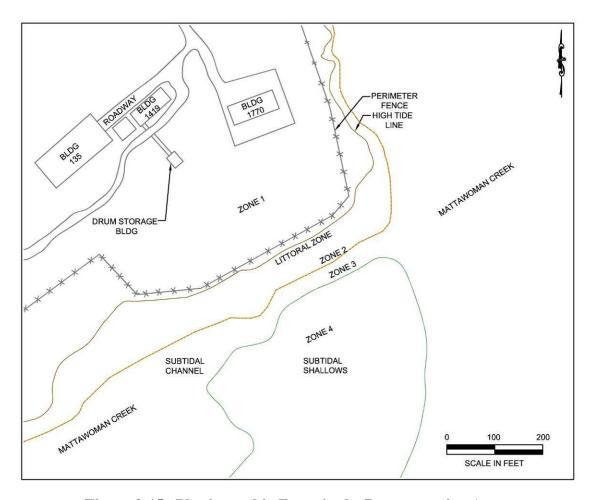


Figure 3-15. Physiographic Zones in the Demonstration Area

3.4.2 Boring and Monitoring Well Installation

An extensive series of groundwater monitoring wells have been installed at the site to evaluate general groundwater conditions and contaminant concentrations. Solutions-IES initial evaluation of site conditions began with evaluating the six monitoring wells (MW-1 through MW-5 and MW-4D) used to monitor the Shaw pilot test. Over the duration of the demonstration, an additional 35 monitor wells and 10 piezometers were installed within the four zones of the site. In order to correlate groundwater levels between wells and the aerial extent of perchlorate in groundwater, the wells were located by survey referenced to mean sea level. **Figure 3-16** shows the network of wells and piezometers installed in the four zones. The well/piezometer construction details are tabulated in **Appendix A**. Additional details of the installation of the network are provided in the following sections. Selected boring logs representing subsurface conditions in the four physiographic zones are included in **Appendix A**.

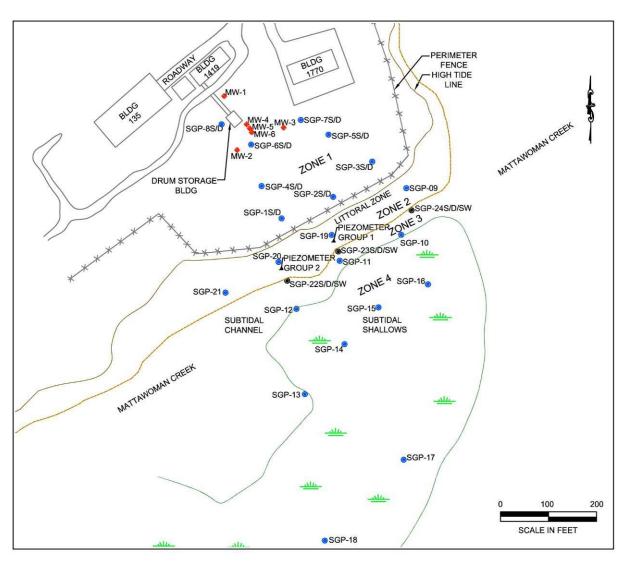


Figure 3-16. Monitor Well and Piezometer Network

3.4.2.1 Zone 1 - Land Borings and Monitor Wells

Eight borings, located upgradient, cross-gradient, and downgradient of the presumed perchlorate source area near MW-1 were opened by a Geoprobe [®] drilling contractor. The soil profile was logged from the boring to establish generalized subsurface conditions. These borings were advanced to 16 to 24 ft bgs, with most terminating in a dark gray clay stratum. Each of these deep borings was then converted to a monitor well with a 2-ft long, 1-inch diameter PVC screen. These wells are denoted with a "D" suffix as "deep" wells. After constructing the deep well at each location, a second Geoprobe boring was opened a short distance away. The offset borings were extended only a few feet below the water table where a second "shallow" PVC well (denoted by the "S" suffix) was constructed. The shallow wells were constructed with 5-foot long well screens set to approximately 15 ft bgs.

3.4.2.2 Zone 2 – Littoral Zone Monitor Wells and Piezometers

Installation of wells and borings in Mattawoman Creek presented unique challenges. Four borings (SGP-9, SGP-19, SGP-20, and SGP-21) were advanced in the Littoral Zone of Mattawoman Creek by driving a Macro-Core sampler using a slide hammer mounted on a tripod. The sampler was recovered after driving and soil contained in the sampler was removed and visually classified. In some borings, sample recovery was minimal because of the soft/loose consistency of the creek sediment. After advancing the borings to termination depths of approximately 8 to 9 ft bgs, a ¾-inch or 1-inch diameter PVC monitor well casing and screen into the boring was pushed into the existing boring before it collapsed. Subsequently, a 4-inch casing was pushed over the monitoring to protect it from the surrounding water.

Piezometers were also installed in the Littoral Zone to evaluate groundwater levels along the creek bank and to evaluate groundwater discharge to the creek bottom by measuring potentiometric head pressures and perchlorate concentrations at different depths. Seven of the piezometers were installed in two locations shown in **Figure 3-16:** three at Piezometer Group 1 and four at Piezometer Group 2. At Piezometer Group 2, TP-4 was screened from 2 to 3 ft bgs, TP-6 was screened from 4 to 5 ft bgs, TP-7 was screened from 5.5 to 6.5 ft bgs and DP-2 was screened from 7 to 9 ft bgs. At Piezometer Group 1, TP-1 was screened from 2 to 3 ft bgs, TP-2 was screened from 4 to 5 ft bgs and TP-3 was screened from 5.8 to 6.8 ft bgs.

The piezometers were constructed of either a 1-ft section of slotted PVC screen and riser or either ³/₄-inch pipe with a 1-ft stainless steel screen. Both types were driven into the sediment by hand with a slide hammer **Figure 3-17**. Two additional piezometers, TP-5 and TP-8, were installed with a hand auger near the creek bank. Piezometers, DP-1 and DP-3 were constructed using steel pipe and stainless steel drive points.



Figure 3-17. Piezometer Installation in the Littoral Zone using a Slide Hammer

3.4.2.3 Zone 3 – Subtidal Channel and Surface Water Monitoring Points

Six monitor wells and three surface water monitoring points were installed by hand as described above in the Subtidal Channel. The locations were accessed using a small boat. These wells were located in three clusters labeled as SGP-22S/D/SW, SGP-23S/D/SW and SGP-24S/D/SW (**Figure 3-16**). Each well cluster consisted of a shallow (S) well screened approximately 2 to 4 feet below the creek bottom, a deep (D) well screened approximately 7 to 8.5 feet below the creek bottom (except SGP-22D), and a surface water (SW) monitoring point from 0 to 1 ft below the creek bottom. The surface water (SW) sampling points were constructed by driving a closed-end section of slotted PVC pipe into the sediment so that the slotted openings were exposed to the water in the creek.

3.4.2.4 Zone 4 - Monitoring Well Installation in the Subtidal Shallows

Solutions-IES installed nine monitor wells (SGP-10 through SGP-18) in the Subtidal Shallows to evaluate pore water conditions within the creek sediment (**Figure 3-16**). Each boring was advanced to a depth of approximately 11 ft below the creek bottom working from a small boat using a slide hammer mounted on a tripod and was later converted to a 1-inch diameter PVC well with a 2-ft screen interval.

3.4.3 Groundwater and Creek Sediment Pore Water Sampling

Water levels were measured in the wells and piezometers prior to the collection of groundwater/pore water samples. When possible, each well that was sampled was purged to remove stagnant water and allowed to recharge from the formation. Because of the anticipated shallow depth to water, the wells were sampled using either a bailer or peristaltic pump. When the monitoring wells were sampled using a low-flow purge and sampling method, an adequate purge was achieved when the pH, specific conductance, and temperature of the groundwater had stabilized as defined in the Technology Demonstration Plan. The parameters measured in wells were altered when necessary in order to collect the volume of sample required for perchlorate analysis.

Purge volumes varied among the wells and piezometers and were noted on the field records. Some wells such as SGP-9 and SGP-20 were noted as being able to produce significant water (five to eight gallons) upon purging. However, most of the site wells and piezometers only produced less than 1 gallon of water before the water level in the well was drawn down into the screen zone.

After an adequate purge was achieved, field measurements were obtained using field meters and groundwater or creek sediment pore water samples were collected for analysis. The field parameters that were typically measured included DO, ORP, pH, temperature and specific conductance. Some of these parameters were not collected if the sample volume was too low.

When groundwater samples were collected using a peristaltic pump, the sample for DO analysis was collected as water flowed out of the sampling tubing by inserting a CHEMetrics® (CHEMetrics, Inc, Calverton, VA) self-filling DO ampoule into the end of the tube. The ampoule tip was broken off inside the tube below the flowing water surface, pulling water into the ampoule while being careful to exclude any air. The DO concentration was determined by a visual comparison to color standards.

3.4.4 Measurement of Hydraulic Head in Wells and Piezometers

Hydraulic head measurements are necessary to understand groundwater flow regimes. Hydraulic head was evaluated in monitor wells and piezometers by direct measurement of the water surface using a water level indicator referenced to the top of the well casing and comparing head values between wells with different screen intervals.

Head measurements were also obtained using three Model 501 Mini-Diver® dataloggers manufactured by Schlumberger Water Services, Waterloo, Canada. Each Mini-Diver® contains a total pressure transducer combined with battery and data recorder capable of storing 24,000 readings. The readings collected include water level, water temperature, date and time. The pressure data are compensated by comparing the water level data to a separate transducer (Baro-Diver® datalogger) placed in a nearby protected location above ground. The Baro-Diver® records atmospheric pressure, air temperature, date and time. Water level readings compensated by subtracting the atmospheric pressure from the total pressure recorded by the Mini-Diver®. Mini-Diver® units were deployed at various times and for varying durations in several wells (SGP-4S, SGP-8S SGP-10D, SGP-21, SDG-23SW/S/D) and piezometers (TP-3, TP-4, RP-5, TP-6 and TP-7).

3.4.5 Determination of Aquifer Hydraulic Conductivity

Aquifer tests were conducted in 14 wells to estimate hydraulic conductivity. Tests included four land wells including SGP-6S, SGP-6D, CPMW-2S and CPMW-2D. The latter two wells were installed in the Control Plot (CP) of the Shaw Pilot Study layout in 2002. They are located approximately 20 feet southeast of the Drum Storage building. Wells in the Littoral Zone included SGP-9, SGP-19, SGP-20 and SGP-21. Wells tested in the Subtidal Channel included SGP-22S and D, and SGP-24S and D. Wells located in the Subtidal Shallows included SGP-10 and SGP-11.

Hydraulic conductivity was estimated by determining the yield of the well while pumping at a measured drawdown (specific capacity) of the well (Wilson et al., 1997). The test uses a peristaltic pump to depress the water level in the well. The measured pump discharge rate (i.e., the well recharge rate at the measured drawdown) is then multiplied by a correction factor to estimate hydraulic conductivity.

3.5 Laboratory Methods

Soil and/or groundwater samples were collected from the land borings/wells, from borings and wells in the Littoral Zone, and in the Subtidal Shallows during five performance monitoring events over a 38-month period. The analytical methods used for each analysis is shown in **Table 3-4.**

Table 3-4 Sample Collection and Analysis Details					
Number of Sample Bottles per Sample Location	Containers	Target Constituent/ Method	Field/ Laboratory		
Groundwater					
1	250-ml plastic bottle	Specific conductivity, temperature, pH, oxidation-reduction potential/ Field Meters	Field		
0	From tubing	Dissolved oxygen/ CHEMetrics TM Field Test Kit	Field		
1	0.45 µm filtered sample	Dissolved manganese and iron/ CHEMetrics TM Field Test Kit	Field		
2	40-mL VOA vial (no preservative)	Methane/gas chromatography	NCSU CCEE Lab* Raleigh, NC		
1	250 ml plastic bottle minimum of 120 ml sample while retaining headspace (no preservative) coupled 1.0μm and 0.45μm filtering setup	Perchlorate/ EPA Method 314 (ion chromatography)	NCSU CCEE Lab Raleigh, NC		
1	A minimum of 120 ml (no preservative) coupled 1.0µm and 0.45µm filtering setup confirmation samples (10%)	Perchlorate/Method 332 (Ion chromatography/ tandem mass spectroscopy)	West Coast Analytical Service (formerly Bodycote) Santa Fe Springs, Ca		
1	250-mL plastic bottle (preservative)	Chloride, Nitrate, Sulfate, Chlorate, Chlorite, Bromide, and Phosphate (ion chromatography)	NCSU CCEE Lab Raleigh, NC		
1	250-mL amber bottle preserved with HCL)	Total organic carbon (groundwater)/Method 9060	Environmental Science Corp. Mount Juliet, TN		
1	1-L amber bottle (no preservative)	Chlorite Dismutase/DNA	Microbial Insights, Inc. Rockford, TN		
Multiple	enzyme filter traps with a minimum flow through of groundwater (500 mL to 1 L)	Molecular Biology Tools: Perchlorate Reductase/DNA	Microbial Insights, Inc. Rockford, TN		
Soil					
1	4-oz jar	Total organic carbon (soil)/EPA Method _415 (Loss on ignition)	Environmental Science Corp., Mount Juliet, TN		

NCSU CCEE Lab = North Carolina State University Civil, Construction and Environmental Engineering Laboratory

3.5.1 Sampling for Standard Analyses

After purging and field sampling as described in Section 3.4.3 above, the samples were collected in laboratory-prepared sample containers appropriate for the analytical method being used. The sample containers were immediately sealed, labeled, and placed on ice in an insulated cooler for subsequent delivery to the analytical laboratory. Chain-of-custody forms accompanied samples sent to the laboratory. Groundwater/sediment pore water samples collected from monitoring wells during performance monitoring were generally analyzed for perchlorate, TOC, chloride, nitrate, sulfate, and methane as well as dissolved iron and manganese. A small subset of the collected samples was also analyzed for chlorite, chlorate, bromide, and phosphate during some sampling events. As shown in **Table 3-4**, most of the analyses were performed using standard field or laboratory methodologies. However, several relatively new approaches were used for collecting and processing samples for perchlorate and microbial testing. These special methods are described in the following sections.

3.5.2 Groundwater Collection for Perchlorate Analysis

The method for collecting aqueous perchlorate samples was described and illustrated in the Perchlorate MNA Protocol (ESTCP, 2008). After the groundwater is withdrawn from the monitoring well or piezometer, solids within the sample were allowed to settle in a closed plastic container. After the sediment had settled, a 60-ml syringe was used to withdraw the sample from the top to avoid solids. Then, the syringe was used to push approximately 30 mL of groundwater through sequentially stacked 1.0 μ m and 0.45 μ m filters into a 40-mL unpreserved VOA vial. The remaining headspace in the vial maintains an aerobic environment to eliminate further bioactivity on the sample; the sample was then placed on ice for shipment. The combination of filtration, an aerobic headspace and cooling has been shown to effectively preserve the samples and provide a representative sample for laboratory analysis. All samples were analyzed for perchlorate at the North Carolina State University Civil, Construction and Environmental Engineering (NCSU-CCEE) Laboratory by ion chromatography similar to EPA Method 314. Approximately 10% of groundwater samples were sent to a subcontract laboratory for confirmatory analysis of perchlorate by EPA Method 332.

3.5.3 Biological Assays –qPCR Analysis

Molecular biology tools (MBTs) provide a sensitive, rapid approach to quantify (i.e., the qPCR assay) specific microorganisms involved with bioremediation. These methods can be applied selectively to detect and/or enumerate the proportion of active perchlorate reducing bacteria in a total population of bacteria. The quantitative polymerase chain reaction (qPCR) method identifies organisms involved with perchlorate reduction by targeting the specific genes found in these organisms: the perchlorate reductase gene (*pcrA*) that codes for the enzyme that mediates the initial breakdown of perchlorate to chlorate and chlorite, and the chlorite dismutase gene (*cld*) that codes for the single enzyme that mediates breakdown of chlorite, the final step in reduction of perchlorate to chloride and oxygen.

The PCR methods can be applied to different genetic material, i.e., RNA-based and DNA-based PCR assays. The RNA-based assay is used to determine the expression of a particular functional gene based upon the abundance of messenger RNA (mRNA). The perchlorate reducing microorganisms use the mRNA to assemble the CD enzyme, and its abundance in the groundwater sample is a direct indication of enzyme activity and, therefore, the active

biodegradation of perchlorate. While RNA is the best indicator of activity, it degrades rapidly and can be lost during field and lab procedures, and therefore, results may be less reliable.

At the time of this project, the DNA-based PCR assays were considered more stable and less subject to sample collection and matrix variability². For this reason, only the DNA-based PCR assays were used during demonstration at the Indian Head site. The methods enabled the selective enumeration of the bacteria capable of dissimilatory perchlorate reduction by targeting a perchlorate reductase gene (*pcrA*) found in the DNA of these organisms. This method provides a direct measurement of the number of active bacteria capable of producing perchlorate reductase.

For DNA based CD analysis, approximately 1 liter of groundwater was collected from selected monitoring wells in bottles provided by Microbial Insights, Inc., placed on ice and forwarded to Microbial Insights, Inc. For perchlorate reductase analysis, Bio-Flo filters provided by Microbial Insights, Inc. were connected in-line with the peristaltic pump tubing during groundwater sampling. The groundwater was allowed to flow through the enzyme filter trap until 0.5-1 L of groundwater had passed through the filter. In some cases the filters became plugged before the required volume of water had passed through the filter. In these cases, an additional filter was used. The exposed filters were capped and the volume of water passing through each was recorded. The filters were shipped under Chain-of-Custody to Dr. Kate Scow at the University of California - Davis for a DNA based analysis of the perchlorate reductase gene (*pcrA*) using qPCR techniques.

3.6 *In Situ* Biodegradation Testing

3.6.1 *In Situ* Columns

In situ columns can be used to evaluate contaminant degradation where there is reasonable expectation that natural attenuation is occurring. Using this procedure, Borden et al. (1997) showed that decay rates measured using *in situ* columns provided a better match with plume-scale degradation rates than conventional laboratory microcosms. The application of *in situ* columns for use with perchlorate sites is discussed in the MNA Protocol (ESTCP, 2008).

Four 6-inch diameter *in situ* columns (IC-1, IC-2, IC-3 and IC-4) were installed in the Littoral Zone at the Indian Head site. IC-1 and IC-2 were installed near Piezometer Group 2. IC-3 and IC-4 were installed near Piezometer Group 1 (**Figure 3-18**). A tripod with gasoline engine operated portable cable drum and casing hammer was carried into the Littoral Zone and set up adjacent to each of the piezometer groups (**Figure 3-19**). Two sections of 6-inch (15-cm) diameter schedule 80 PVC pipe were driven into the creek sediment using the casing hammer. The deeper columns (IC-1 and IC-3) were driven to a depth approximately 6.5 feet below the creek bottom (mudline). The shallower columns (IC-2 and IC-4) were driven approximately 3 ft below the creek bottom. The top of each casing was left approximately 6 inches above grade.

-

² Personal communication, Microbial Insights, August 2008

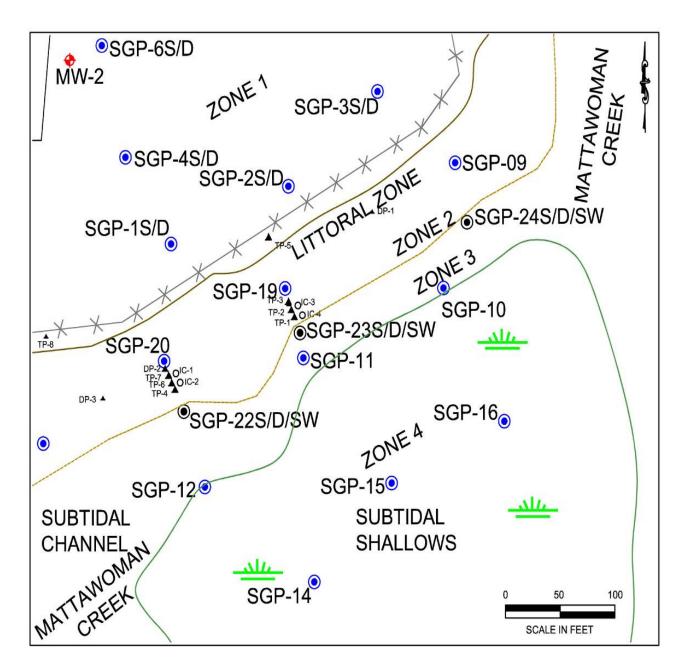


Figure 3-18. In situ Column Locations in the Littoral Zone

A 6-inch section of 1-inch PVC well screen was installed inside the PVC casing just below the bottom so that water samples could be collected from the interior of the 6-inch pipe (**Figure 3-19**). Both the 1-inch and 6-inch casings were then extended approximately 3-ft above grade and capped with a vented well cap. A plastic check valve was installed in the 6-inch casing at the mud line to allow water accumulating within the larger casing to drain during periods of low tide. The design of the check valve was to prevent an inflow of surface water during high tide. However, the check valves became damaged during freezing weather and were eventually removed from all the columns. Surface water appeared to be leaking into the short columns, IC-

2 and IC-4 during initial testing, so additional testing utilizing these columns was discontinued. The biodegradation study continued with the deeper *in situ* columns, IC-1 and IC-3.



Figure 3-19. In Situ Columns IC-3 and IC-4 adjacent to Piezometer Group 1

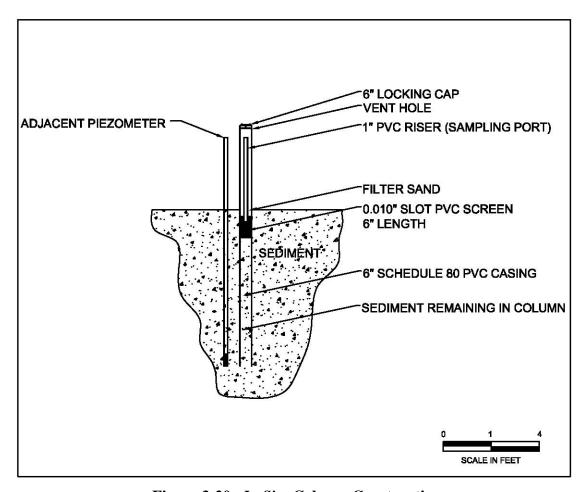


Figure 3-20. In Situ Column Construction

The *in situ* columns were designed to allow water contained in the sediment to flow upward through the columns, but to minimize surface water infiltration during testing. By analyzing water from an adjacent deeper piezometer for the perchlorate concentration and measuring perchlorate concentration inside the top of the column, it was possible to evaluate if biodegradation of the perchlorate was occurring as groundwater containing perchlorate moves upward through organic rich sediments. A discussion of the results of the *in situ* column biodegradation study is provided in Section 6.3.2. A discussion of groundwater flow conditions at the site that influenced the design and placement of the columns in Section 4.0.

3.6.2 Macrocosms

The microcosm studies performed during the site selection process used soil and groundwater from wells closer to the source in Zone 1. Although these were useful for demonstrating the potential for perchlorate MNA to occur, they did not provide direct evidence of bioactivity in the Littoral Zone (Zone 2), where the majority of biodegradation was presumed to be occurring. For this reason, macrocosms were constructed during the demonstration to evaluate perchlorate biodegradation using soil collected from the Littoral Zone instead of sediment from a land well. To construct the macrocosms, soil was collected from the middle of the Littoral Zone downgradient from SGP-2D. Plant material was removed from the soil, and approximately 85 pounds of soil were removed from a depth of approximately 6 to 30 inches bgs, and randomly placed into five different plastic tubs. The plastic tubs weighed approximately 17 pounds each.

The collected soil was mixed by hand in large plastic tubs until homogenous and large rocks (>0.5 inch diameter) were removed from the soil using a decontaminated spoon or gloved hand. The soil was transferred into separate 5-gallon carboys (**Figure 3-21**). Each carboy was filled approximately half full with groundwater from nearby monitor well SGP-2D while minimizing sample aeration. Air from both the carboy and well were evacuated using argon gas. Once all of the soil was added, the carboy was agitated to release air bubbles, filled completely with groundwater from SGP-2D, and sealed without air bubbles. The carboys were labeled and transferred to the NCSU-CCEE laboratory for incubation and monitoring. Groundwater samples were collected periodically from each macrocosm and tested for chlorite, chloride, nitrite, chlorate, bromide, nitrate, sulfate, phosphate, and perchlorate. Six replicates were prepared. The results are discussed in Section 6.3.1.



Figure 3-21. Preparing Macrocosms in 5-Gallon Carboys

3.6.3 Stable Isotope Analysis

Isotopic ratios of chlorine and oxygen atoms in perchlorate (35 Cl/ 37 Cl and 16 O/ 18 O) can be used as a tool to measure the extent of perchlorate degradation. Stable isotope analysis provides a method for distinguishing biotic from abiotic attenuation. It appears that dissimilatory perchlorate reducing bacteria (DPRB) microorganisms often preferentially use lighter isotopes in their metabolic processes (Coates and Achenbach, 2006). As perchlorate is degraded, the isotopic composition fractionates significantly and the remaining material becomes progressively heavier (Sturchio et al., 2003; McKelvie et al., 2007). If there is clear evidence of an isotopic shift, the extent of perchlorate degradation can estimated using the fractionation factor. If there is no change in the isotopic ratio despite a change in concentration, then it may be concluded that the attenuation mechanism is abiotic.

Compound specific isotope analysis (CSIA) requires collection of approximately 10 mg of perchlorate in the sample trap from groundwater from locations where conditions suggest that perchlorate may be biodegrading as well as background locations. The large volume of groundwater necessary to perform stable isotope studies could not be practically obtained from the Littoral Zone where perchlorate concentrations were slightly above detection limits and groundwater recharge was slow. Therefore, CSIA was not conducted at the Indian Head site.

3.7 Residuals Handling

Several types of investigation-derived waste (IDW) were generated on this site including:

- Personnel protective equipment (PPE).
- ➤ Disposable equipment, such as plastic ground and equipment covers, aluminum foil, tubing, bailers, discarded or unused sample containers, boxes, etc.
- ➤ Soil cuttings/Geoprobe[®] Macro-core[®] liners.
- > Groundwater/sediment pore water obtained through well development/well purging.
- > Decontamination fluids including detergents and wash water.
- Packing and shipping materials.

Based on NSWC (generator) knowledge, the IDW was classified as non-hazardous. Soil cuttings were spread on site in the grassed area south of the Drum Storage building. Groundwater and sediment, as well as fluids derived from well sampling and equipment decontamination, were also disposed of on the land surface in the grassed area south of the Drum Storage building. Solid waste, such as PPE, bailers, tubing, in-line filters, etc., was double-bagged and deposited in a dumpster for transport to a municipal landfill.

4.0 Site Area Hydrogeology

4.1 Regional Hydrogeology

The town of Indian Head and the NSWC are located on a narrow peninsula of land bounded to the north by the Potomac River and to the south by Mattawoman Creek. Both the Potomac River and Mattawoman Creek are part of the Chesapeake Bay estuary system and are tidally influenced with an average diurnal tide change of less than 1 foot.

According to Hiortdahl (1997), the study area lies within the Coastal Plain Physiographic Province of Maryland approximately 50 miles from its western-most limit. The coastal plain has been formed by the deposition of a sequence of easterly dipping sediments on top of crystalline bedrock. In the vicinity of Indian Head, these sediments are approximately 700 feet thick. They have been mapped (from oldest to youngest) as the Potomac Group, which include the Patuxent, Arundel, and Patapsco formations. The Patapsco formation is overlain by an unnamed sequence of Tertiary-aged deposits, which are in turn, overlain or replaced by Miocene to Pleistocene age fluvial (river) and estuarine (estuary) sediments. During the Pleistocene, multiple periods of glaciation resulted in rivers and streams incising new or deeper channels as sea levels dropped. During these periods, the eroded channels of the Potomac River and its tributaries may have been 60 to 90 feet below their current levels. The eroded channels have now refilled with river and estuary sediment.

The cross-section in **Figure 4-1** is oriented in a general north to south direction and passes a few miles west of the town of Indian Head. Tertiary-aged sediments are limited to the bluff on the south side of the Potomac River. The former paleochannels of Potomac River and Mattawoman Creek that were eroded into the Patapsco Formation are shown filled with recent sediment.

In the Indian Head area, the Patuxent and Patapsco formations are highly productive aquifers furnishing water of good quality to wells supplying NSWC, the Town of Indian Head, and other municipalities in the area. The Patuxent is confined by the overlying clay of the Arundel Formation and the Patapsco Formation is confined by upper clay beds.

Long-term groundwater use in the vicinity of Indian Head has lowered the hydraulic head in both the Patapsco and Patuxent aquifers. Hydraulic head levels measured in 1989 (the most recent data available) for wells screened in the Patapsco and Patuxent aquifers in the vicinity of the NSWC were 60 to 90 feet below sea level (Hiortdahl, 1997). Increasing chloride concentrations in some wells located in the northern half of the Indian Head peninsula along the Potomac River suggests the Patapsco aquifer and to a lesser extent the Patuxent aquifers are being recharged from the brackish water of the Potomac River through the river bottom sediment.

As opposed to the deeper confined Patapsco and Patuxent aquifers, the surficial (water table) aquifer is unconfined and consists of a relatively thin layer of saturated alluvial soil resting on top of the clayey confining unit of the Patapsco Formation. The water table surface generally slopes similarly to the overlying land surface topography and varies in its vertical position seasonally in response to changes in precipitation and evapotranspiration. Infiltration of precipitation falling within upland areas recharges the surficial aquifer. Some water in the surficial aquifer recharges the underlying confined aquifer, but this recharge is restricted by the

low conductivity of the Patapsco clay, with the result that most of the surficial aquifer discharges to seeps, springs, creeks, and rivers.

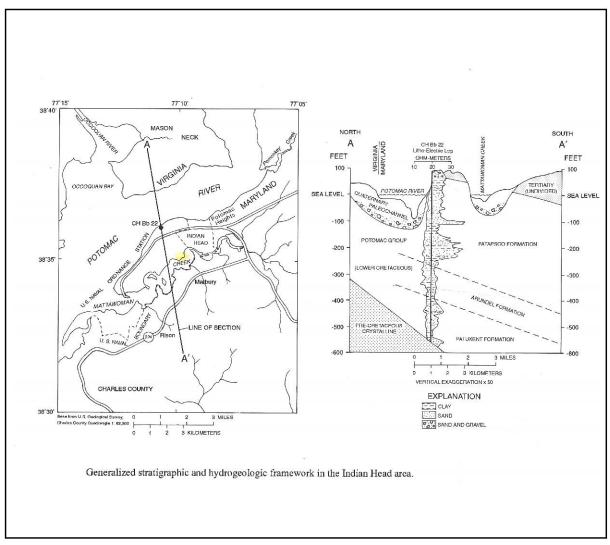


Figure 4-1. Generalized Stratigraphic and Hydrologic Framework of the Indian Head Area (Source: Hiortdahl, 1997)

4.2 Local Subsurface Conditions

The Project Area is located within the eastern part of the NSWC, in the vicinity of Building 1419. The area south of Building 1419 was investigated by Shaw and others in 2002 as part of a pilot test to study the effects of *in situ* biodegradation of perchlorate. Between 2005 through 2007, Solutions-IES installed a network of 35 monitoring wells and 10 piezometers beginning approximately 150 feet south of Building 1419 and extending in a southerly direction into Mattawoman Creek (**Figure 3-16**).

The following subsections describe hydrogeologic conditions within each of the four zones. Zone 1 and possibly upper portions of Zone 2 during low tide are the only zones where

unsaturated soil conditions and a water table exist. The sediment in Zones 3 and 4 is completely saturated.

4.2.1 Subsurface Conditions in the Site Area

Figure 4-2 shows Section A-A' oriented in a north to south direction through the site. The section shows the generalized subsurface conditions extending from the vicinity of the drum storage pad into Mattawoman Creek. Detailed sections B-B' and C-C' oriented north to south through the Littoral Zone (**Figure 4-3 and 4-4**) were constructed to better defined hydrogeologic conditions as perchlorate impacted groundwater discharges through the Littoral zone. As part of this work, a variety of wells and piezometers were installed to evaluate water quality parameters and head pressure variations at different depths within the Littoral Zone sediment. Selected borings logs are included in **Appendix A.**

In previous work, Cramer et al. (2004) described fill soils having been previously placed in various areas of the site. The fill was described as gravel and silty sand containing some organic matter and debris its thickness ranged from less than a foot to approximately 4 feet in thickness. Underlying the fill is 13 to 16 feet of silty sandy-sandy silt containing thin (1 inch to 2 inches thick) discontinuous sand lenses (stringers). The units vary both horizontally and vertically and rest on 12 to 18-inches of coarse alluvial sand and gravel. The coarse alluvium also appears to be variable in thickness and location.

Solutions-IES also identified similar subsurface conditions to be present south of the limit of the Shaw borings. However, the coarse alluvium was not identified in two borings, SGP-2D and SGP-3D located closer to Mattawoman Creek. At these locations, the basal portion of the alluvium consists of fine-grained sand without the gravel. The alluvium rests on dark gray clay, which extends to a depth of at least 24 ft bgs at SGP-2D. The clay, encountered beneath the alluvium in the land borings appears to be extensive and has been identified at other locations within NSFC. Site #57 (Tetra Tech NUS, 2000) also describes the presence of a clay unit beneath alluvium and fill that restricts downward groundwater flow. Based on visual characteristics of the recovered samples, the clay is inferred to be the eroded surface of the Patapsco confining unit.

Borings advanced in the creek were generally terminated at shallow depths of 10 to 11 feet or less. The creek sediments were found to consist of several feet of organic muck (silt and clay) containing an abundance of decayed plant matter underlain by greenish tan to gray silty to clayey fine sand. The soft or loose consistency of the sediments made their recovery using a split spoon difficult. The Patapsco clay that was encountered near the termination of the land borings was not identified in the creek. This may be due to the relatively shallow depth of the borings in the creek and the downward sloping eroded surface of the Patapsco unit.

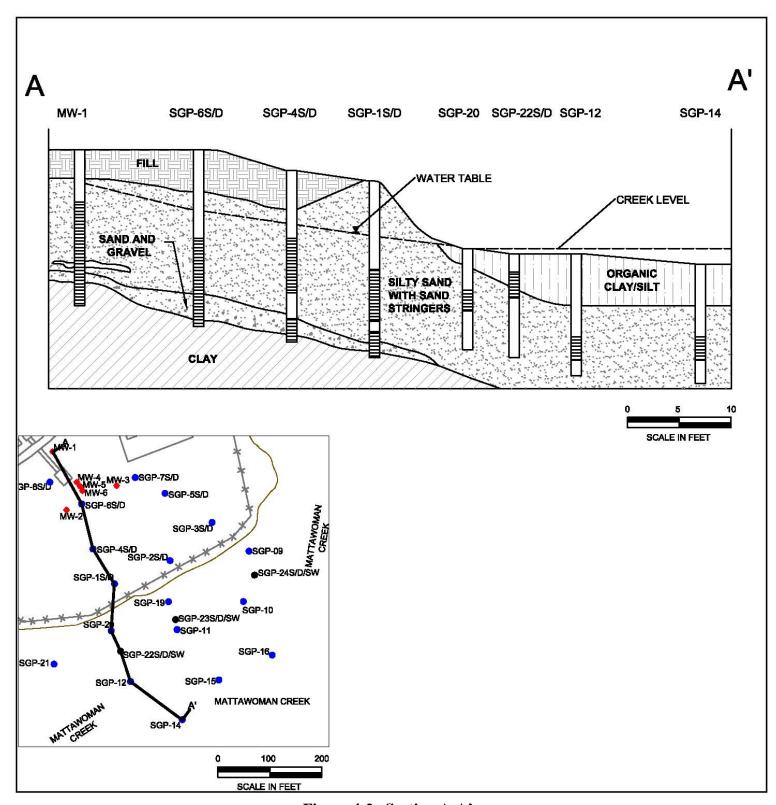


Figure 4-2. Section A-A'

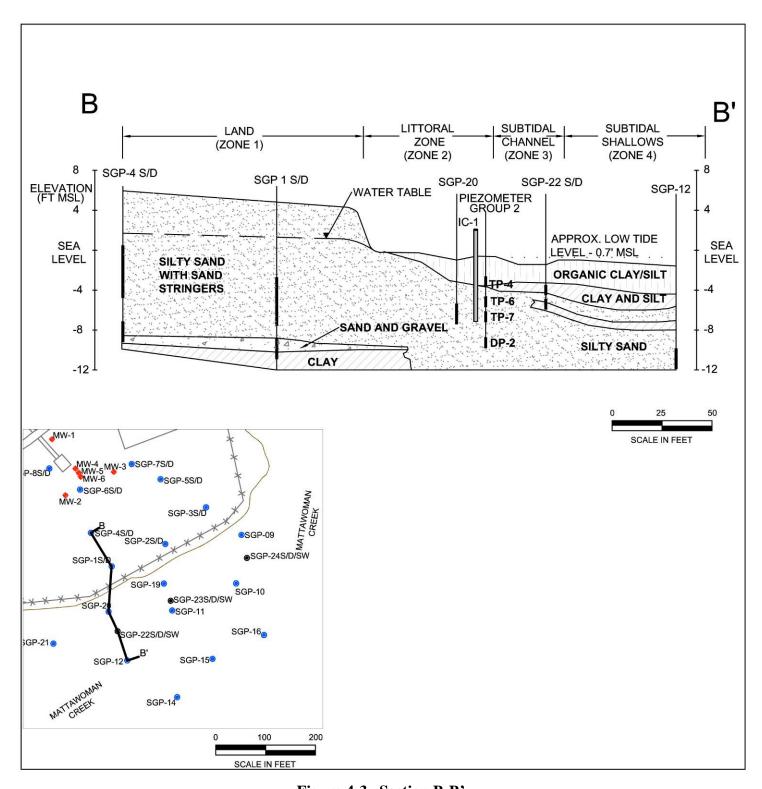


Figure 4-3. Section B-B'

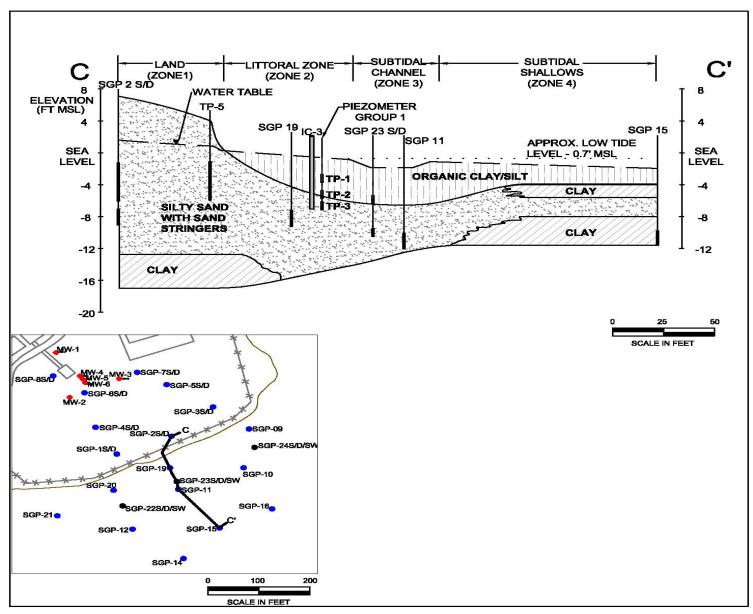


Figure 4-4. Section C-C'

4.2.2 Hydraulic Conductivity of the Surficial Aquifer

As described in **Section 3.4.5**, aquifer tests were run on 14 wells to determine the hydraulic conductivity (K) of the surficial aquifer and adjoining sediments (**Table 4-1**). The average and range of K in each of the four zones is presented in **Table 4-2**. K values in zones 1 to 3 varied from 0.1 to 15 ft/d with an average of 5 ft/d, with no clear difference in the average permeability of the different zones. Measured K in the Mainland Zone is generally consistent with previous reports (ESTCP, 2006; Tetra Tech NUS, 2000). K for the Mainland and Subtidal Channel wells were variable, presumably due to zones of coarser or finer grained alluvium. In contrast, K for the Littoral Zone wells was much less variable.

In contrast to zones 1 to 3, K values in the Subtidal Shallows were significantly lower (average K = 0.07 ft/d). The relatively low conductivity of these sediments was borne out during sampling, where most of the wells produced little water before being dewatered.

Table 4-1 Aquifer Tests Results						
Well	Well	Horizontal				
Number	Depth (ft bgs)	Elevation (ft msl)	Hydraulic Conductivity (ft/d)			
Zone 1 - Mainland						
SGP-6S	8.5 to 13.5	0.26 to - 4.74	0.5			
SGP-6D	13.8 to 15.8	-5.09 to -7.09	0.1			
CPMW-2S	4.0 to 11.0	5± to 2±	7.6			
CPMW-2D	10.5 to 13.5	-0.5 to -4.5	12.4			
Zone 2 - Lit	Zone 2 - Littoral Zone					
SGP-9	6.1 to 8.1	-7.1 to -9.1	2.3			
SGP-19	6.7 to 8.7	-7.2 to -9.2	2.1			
SGP-20	4.2 to 6.2	-5.3 to -7.3	2.5			
SGP-21	2.7 to 7.7	-3.9 to -8.9	3.8			
Zone 3 - Subtidal Channel						
SGP-22S	1.8 to 2.8	-3.5 to -4.5	11.3			
SGP-22D	3.2 to 4.2	-4.9 to -5.9	0.5			
SGP-24S	2.9 to 3.9	-4.3 to -5.3	14.9			
SGP-24D	7.6 to 8.6	-9.0 to -10.0	7.2			
Zone 4 - Subtidal Shallows						
SGP-11	8.0 to 10.0	-10.1 to -12.1	0.06			
SGP-10	8.4 to 10.4	-10.4 to 12.4	0.08			

ft bgs = feet below ground surface ft msl = feet above mean sea level

ft/d = feet per day

Table 4-2 Average and Range of Horizontal Hydraulic Conductivity in Zones 1 to 4					
Zone	Hydraulio	Hydraulic Conductivity (ft/d)			
	Average	Range			
1 – Mainland	5.2	0.1-12.4			
2 – Littoral	2.7	2.1-3.8			
3 - Subtidal Channel	8.5	0.5-14.9			
4 - Subtidal Shallows	0.07	0.06 - 0.08			

4.3 Groundwater Flow at the Site

Perchlorate is present in the surficial, water table aquifer at the site and is migrating generally south-eastward towards Mattawoman Creek. During several performance monitoring events, depth to water was measured in wells and piezometers; results are tabulated in **Appendix B.** There is one or more deeper confined aquifer(s) present within the Patapsco and underlying formations. However, these aquifers are separated from the surficial aquifer by the Patapsco clay confining unit and not believed to be impacted by the perchlorate release. All wells constructed at the site are screened in the surficial aquifer and no site-specific information has been developed for the deep aquifers.

4.3.1 Groundwater Flow in Zone 1 - Mainland

Saturated soils are encountered between 6 and 10 ft bgs south of Building 1419. The surficial aquifer is thin, only 10 to 12 feet in thickness, with the base defined by the Patapsco clay. The water table surface slopes and the depth to the water table decreases to the south and east toward Mattawoman Creek. **Figure 4-5** shows the water table surface as a series of contours as determined from measurements obtained in the site wells in April 2008. The average water table slope (horizontal hydraulic gradient) as measured between wells MW-1 and SGP-2S is approximately 0.018 ft/ft. This is in general agreement with previous monitoring results at the site (Cramer et al., 2004) indicating a gradient of 0.023 ft/ft.

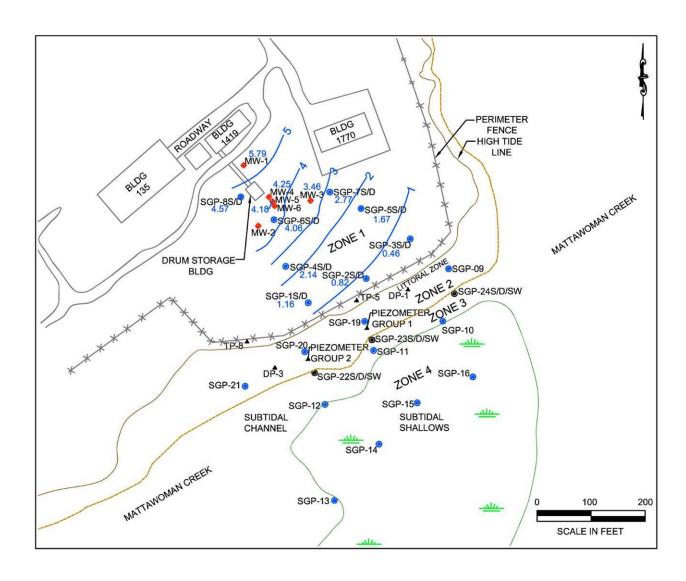


Figure 4-5. Water Table Contour Map (April 2008)

4.3.2 Groundwater Flow in Zones 2 and 3 – Littoral Zone and Subtidal Channel

Groundwater flow patterns in zones 2 and 3 are complicated by spatial variations in permeability and tidal fluctuations in Mattawoman Creek. On average, groundwater from the mainland flows the east-southeast and discharges to the Littoral Zone and Subtidal Channel. The Littoral Zone is a relatively narrow fringe along the creek bank that is covered by water during high tide and exposed during low tide. During low tide, the top few inches of sediment along the high tide line may drain and become partially saturated during low tide, exhibiting a "water table" a few inches below the land surface. The partially saturated zone disappears during the next high tide.

Groundwater discharge to receiving streams has been shown a source of nutrients and agricultural pesticides (Li and Jiao, 2003). Quantification of solute transport effects in coastal aquifer systems and the tidal effects on submarine groundwater discharge and beach hydraulics is challenging because of non-linearity resulting from water flow in the unsaturated zone (Li et al., 2008). At Mattawoman Creek, the discharge area likely varies in its width and distance from

the creek bank daily and seasonally according to tidal levels in the creek. At ebb tide, the beach water table may be decoupled from the creek resulting in the formation of a seepage face where groundwater seeps onto the intertidal profile (Uchiyama, 1999). Li et al. (2008) also noted that the major portion of the outward groundwater seepage usually occurs in the shallow part of the submerged beach and the magnitude decreases with distance from the shore. They concluded that on average, the outflow from the seepage face accounts for about half the outflow from the intertidal zone. Groundwater discharge probably ceases during high tide when water in creek recharges the shallow creek sediment. These local circulation cells are formed in the aquifer near the shoreline as a result of tidal fluctuations and the salinity profile is attributable to this circulation (Uchiyama, 1999; Li and Jiao, 2003). The Subtidal Channel probably acts as a collector routing seepage from the edge of the Littoral Zone to the creek channel west of the study area. Based on distance from shore, little groundwater is expected to discharge to the Subtidal Shallows area.

To gain a better understanding of these flow patterns, piezometers were installed at several locations and depths in Zones 2 and 3 and monitored for changes in pressure head with time. Figure 4-6 shows the variation in water levels in Piezometer Group SGP-23 installed in the Subtidal Channel from late October to early November 2006. SGP-23SW was installed to monitor surface water elevations in the Subtidal Channel. The creek bottom at this location is approximately 2.1 ft below msl. SGP-23D is screened from 9.5 to 10.5 ft below msl (7.4 to 8.4 feet below the creek bottom) and was designed to monitor water levels deeper in the aquifer. From 10/24 to 10/26, there were typical diurnal tides which resulted in a 0.4 to 0.8 ft fluctuation in water levels in the Subtidal Channel. Pressure fluctuations deeper in the aquifer lag the surface water by 1 to 2 hours and were much more muted with head variations of a few hundredths of a foot, suggesting the aquifer at this location behaves in a semi-confined condition. During low tide periods, the head in the aquifer is greater than in the surface water and flow is upward. However, during high tides, head in the surface water is greater, resulting in some flow reversal and the potential for surface water to enter the aquifer. The actual amount of surface water that enters the aquifer is probably limited due to the semi-confined condition. On average, there appears to be a net flow of water from the aquifer into surface water. This discharge was commonly observed during low tide as small seeps and flowing rivulets of water. Creek water re-saturates the surficial sediment on the next rising tide; reducing the hydraulic gradient and slowing groundwater discharge to the creek.

Mattawoman Creek periodically experiences significant wind driven tides. During Oct 27-28, 2006 wind driven tides caused the water level in Mattawoman Creek to rise over 2 feet above normal, resulting in a strong hydraulic gradient from the surface into the aquifer for 1 to 2 days. Once the high wind period ended, water drained out of Mattawoman Creek and there was a period of unusually low surface water levels with a strong hydraulic gradient from the aquifer to surface water. These flow reversals likely result in some mixing of surface and groundwater. However, the exact amount of water that enters the aquifer during flow reversals is impossible to estimate without precise measurements of vertical hydraulic conductivity. In Section 6, field monitoring results will be presented showing that pore water within deeper sediment has chemical characteristics similar to groundwater in Zone 1 – low chloride concentrations and slightly acidic pH. This indicates that mixing of surface and groundwater is limited to the upper few feet of the Littoral Zone and Subtidal Channel.

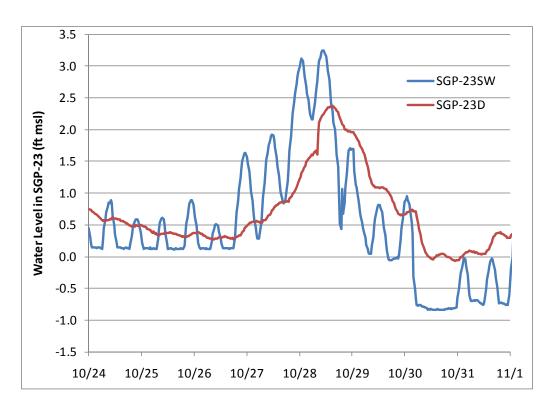


Figure 4-6. Variation in Water Elevations from Oct. 24 to Nov. 1, 2006, in Piezometer Group SGP-23 Installed in the Subtidal Channel

4.3.3 Groundwater Flow in Zone 4 - Subtidal Shallows

Groundwater monitoring in the Subtidal Shallows (Zone 4) showed very different chemistry with high levels of methane, dissolved iron and chloride indicating groundwater in this area does not actively communicate with the mainland. This is reasonable to expect given the low hydraulic conductivity of this material and absence of a hydraulic gradient to transmit groundwater.

4.3.4 Groundwater Discharge Rates

To gain some understanding of the groundwater discharge rates, water levels in Piezometer Groups 1 and 2 were monitored during low tide periods on three occasions in 2007 and 2008. During low tide, the creek bottom was exposed indicating the piezometric surface was equal to the creek bottom elevation. The depth to water was measured in the piezometers using an electronic water level indicator. In all cases, water levels in the piezometers were above the creek bottom indicating an upward hydraulic gradient.

Figure 4-7 shows computed hydraulic gradients between different elevations in Piezometer Groups 1 and 2. Gradients were calculated by dividing the difference in measured water levels by the distance from the center of one screen to the next. Salinity levels in the creek and sediment are less than 250 mg/L, so density corrections were not required. The legend indicates the vertical interval used to calculate the gradient so 'GP1: 0-2.5 ft' indicates the hydraulic gradient from 0 to 2.5 ft below the creek bottom in Piezometer Group 1.

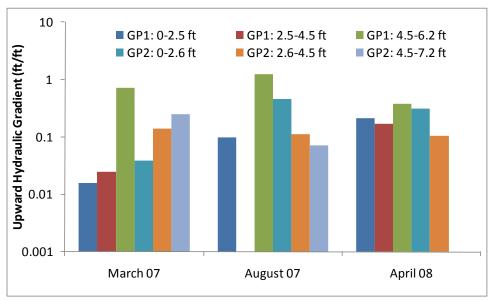


Figure 4-7. Measured Hydraulic Gradients between Different Depths in Piezometer Groups 1 and 2 on Three Dates

Average hydraulic gradients observed over the three different monitoring dates varied from 0.07 to 0.77 ft/ft, with an overall average of 0.24 ft/ft. All hydraulic gradients were upward from the aquifer to surface water, as expected for low tide periods. In Piezometer Group 1, hydraulic gradients were consistently higher in the 4.5 to 6.2 ft depth interval, implying the presence of a more restrictive layer underlying the shallow organic rich sediments where pressures dissipate more rapidly. In contrast, the hydraulic gradients in Piezometer Group 2 were more consistent and do not indicate the presence of a restrictive layer.

A standard approach is to compute velocity (v) using Darcy's Law [v = K ($\Delta H/\Delta L$)/n] where K is hydraulic conductivity, $\Delta H/\Delta L$ is hydraulic gradient, and n is porosity. Horizontal hydraulic conductivity (K_H) in the Littoral Zone and Subtidal Channel was measured in eight separate wells/piezometers and varied from 0.5 to 14.9 ft/d with an average of 5.6 ft/d. Assuming the vertical hydraulic conductivity (K_V) is 10% of average K_H and porosity is 0.25, the average vertical velocity during low tide would be 0.5 ft/d. For an average low tide period of 6 hr, groundwater would migrate upward up to 1 to 2 inches (2.5 to 5 cm), before the tide changes and flow reverses. During a 2-day period of wind-driven high tides, the average hydraulic gradient downward might be 0.1 to 0.2 ft/ft (**Figure 4-7**) and the average downward migration of surface water into the aquifer would be 6 to 12 inches.

4.4 Geochemical Indicators of Groundwater Flow Patterns

4.4.1 Temperature

Temperatures in surface water at the Indian Head site vary daily and seasonally. Pressure transducers installed in selected wells in October 2006 to measure tidal fluctuations also measured water temperature. The surface water temperature (SGP-23SW), shallow pore water (SGP-23S), and deeper pore water (SGP-23D) measured for the first week in October 2006 are shown in **Figure 4-8**. The shallow piezometer (SGP-23S) responds rapidly to changes in surface water temperature. In contrast, the deeper piezometer (SGP-23D) is not affected by changes in surface water temperature, indicating the deeper zone does not rapidly exchange water with the surface.

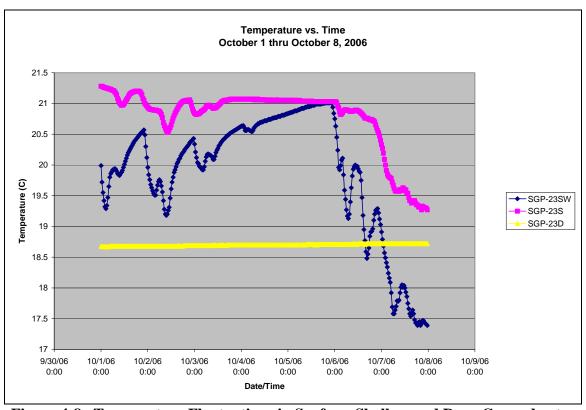


Figure 4-8. Temperature Fluctuations in Surface, Shallow and Deep Groundwater

4.4.2 Chloride

Chloride concentrations are relatively low in the Mainland wells (typically 5 -30 mg/L) and increase to the southeast towards Mattawoman Creek. Chloride levels in the Potomac River and Mattawoman Creek can vary significantly due to precipitation events and wind-driven tides (Hiortdahl, 1997). Surface water monitoring data collected during this study showed surface water chloride concentrations varying from 27 to 364 mg/L with an average of 148 mg/L (std. dev. = 143 mg/L, n=11).

Figure 4-9 shows chloride concentrations (mg/L) in March 2007 plotted in different sampling locations throughout the site. Chloride concentrations in the land wells are generally less than 25

mg/L. In the Littoral zone, there appears to be two groups of wells: (a) deep wells with chloride concentrations similar to the land wells; and (b) shallow wells with somewhat more elevated chloride concentrations due to recharge of surface water with elevated chloride. The Subtidal Channel wells all have elevated chloride concentrations indicating a major impact from surface water recharge. The Subtidal Shallows wells had the highest chloride concentrations observed in March 2007, indicating no significant exchange with the land aquifer.

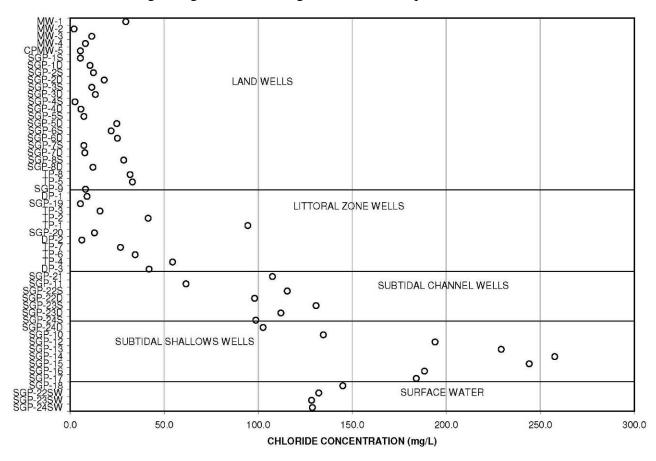


Figure 4-9. Chloride Concentrations in March 2007 at Different Sampling Locations

Figure 4-10 shows vertical profiles of chloride concentration versus depth on several dates in the Littoral Zone Piezometer Groups 1 and 2, and the Subtidal Channel wells SPG-23 and SPG-24. In both Piezometer Group 1 and 2, there is a steady decrease in chloride concentration with depth below the land surface on every sampling date indicating relatively limited mixing of surface water and groundwater in deeper portions of the Littoral Zone. In contrast, chloride concentrations are high at all depths in SPG-23 and SPG-24 on every date indicating extensive mixing of surface water and groundwater in the Subtidal Channel.

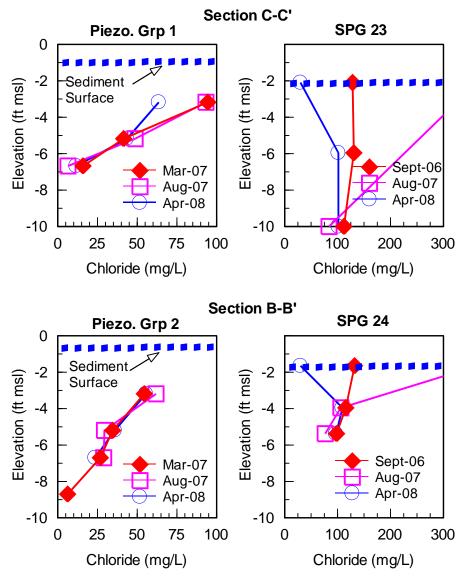


Figure 4-10. Vertical Profiles of Chloride Concentration vs. Depth in Littoral Zone (Piezometer Groups 1 and 2) and Subtidal Channel (SPG-23 and SPG-24).

4.4 Generalized Hydrogeologic Model

A general conceptual groundwater flow model was formulated for the surficial aquifer at the site based on a groundwater compartment that extends from the topographic high north of Building 1419 to the Littoral Zone within Mattawoman Creek. The base of the compartment occurs at the top of the Patapsco confining unit. With the exception of minor seepage that occurs into the Patapsco confining clay, groundwater within this compartment will eventually discharge to Mattawoman Creek. The deeper confined Patapsco aquifer has not been included in the conceptual model because the low hydraulic conductivity of Patapsco clay restricts recharge of the underlying confined aquifer to a small percentage of the water contained in the surficial aquifer.

Fill and alluvium rest on the eroded surface of Patapsco clay. The base of the alluvium consists of a layer of sand and gravel that have been eroded from upland areas. This is in turn, covered with silty and clayey sand containing sand lenses (stringers). In Mattawoman Creek, the top of the Patapsco has been scoured downward and a thick accumulation of silty sediment has been deposited by the creek as it has meandered within its flood plain. Because of the wetland vegetation present along both sides of the creek channel, the creek sediment is now capped with several feet of soft silty clay (muck) containing abundant decayed organic matter.

Precipitation infiltrates to the water table in the higher land elevations within the study area and to the north. Shallow groundwater in the study area moves toward the south toward the creek. Upon entering the creek sediments, groundwater tends to migrate upward and discharges to the creek within the Littoral Zone and Subtidal Channel. At the creek bank the hydraulic gradient of the aquifer provides the driving force for groundwater discharging through the nearshore sediment to the creek. Short term changes in the gradient occur through tidal loading. This oscillatory change in gradient directly affects the rate of discharge to the creek. Groundwater discharge decreases even ceasing during periods of high tide when water in creek tend to infiltrate and recharge the shallow creek sediment. This cyclic discharge/recharge tends to increase residence time and results in additional dilution and mixing within the shallow creek sediments (Westbrook et al., 2005; Robinson et. al., 1998).

The Subtidal Channel acts as a surface water collector routing seepage from the Littoral Zone to Mattawoman Creek through an outlet west of the study area. The minimal thickness of the surficial aquifer and very low conductivity of the sediment within the Subtidal Shallows restrict groundwater discharge to the Littoral Zone.

Figure 4–11 shows a flownet developed for the study area based on water levels measured in April 2008. The construction suggests that the gradient flattens from the vicinity of Building 1419 toward the creek and that groundwater has slight radial flow as the flow tubes diverge to the south. Assuming a uniform saturated thickness of 10 ft and horizontal hydraulic conductivity of 5 ft/d, the average discharge from the aquifer to the Littoral Zone/Subtidal Channel would be approximately 300 ft³/day (2,244 L/day). Visual observations of the discharge face during low tide indicates the discharge face is between 50 and 100 ft wide. 300 ft³/d of discharge would then result in an average upflow velocity in the discharge area of 0.04 to 0.08 ft/d. Organic rich sediments in the Littoral Zone are 2 to 4 ft thick which would result in an average residence time in this organic rich zone of 25 to 100 days.

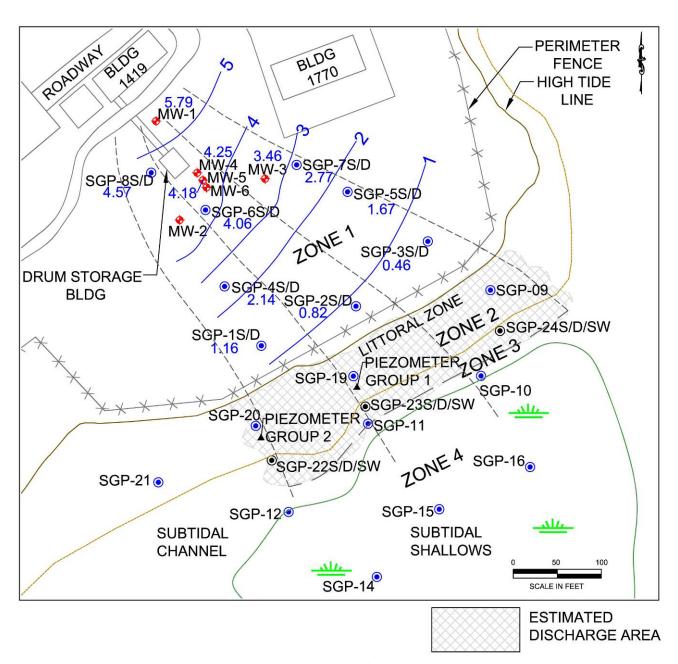


Figure 4-11. Flow Net for Study Area

5.0 Conceptual Model of Perchlorate Transport and Fate

At the Indian Head site, perchlorate concentrations in groundwater exceed the MDE Drinking Water Standard of $2.6 \,\mu\text{g/L}$. This section presents a general conceptual model for the transport and natural attenuation of perchlorate as it migrates from the source area towards and into Mattawoman Creek.

As described in Section 4.4, groundwater is believed to enter the shallow aquifer as diffuse recharge in upland areas of the site. Building 1419 is reported to have been used to clean out or "hog-out" solid propellant containing ammonium perchlorate from various devices, including rockets and ejection seat motors. This process is thought to have resulted in the discharge of solid perchlorate and/or water containing perchlorate on the soil surface in the general vicinity of Building 1419. Perchlorate present in the soils would then be carried vertically into the shallow water table aquifer by infiltrating rainwater. Sorption of perchlorate to the aquifer matrix is believed to be minimal, so perchlorate could be flushed from the aquifer relatively easily by ambient groundwater flow.

The exact location of the hog-out activities is not known, but is believed to have occurred in the general vicinity of Building 1419 in the northwestern portion of **Figure 5-1**. Elevated concentration of perchlorate in SGP-8 and TP-8 suggest that perchlorate may have entered the aquifer in areas south of the drum storage building. However, the focus of this study is on the transport and fate of perchlorate that entered the aquifer from a 'source area' in the general area of MW-1, MW-3 and MW-4.

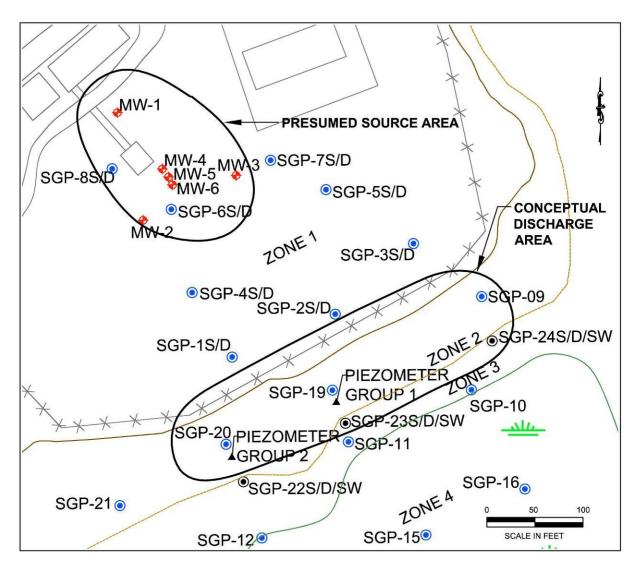


Figure 5-1. Presumed Source and Conceptual Discharge Areas

As groundwater migrates from the source area downgradient to the southeast towards Mattawoman Creek, perchlorate concentrations appear to gradually decline with distance. This decline is believed to be due to dilution with uncontaminated groundwater and, possibly, some biodegradation. The underlying Patapsco clay restricts downward movement of dissolved perchlorate so most of the remaining perchlorate mass moves horizontally towards Mattawoman Creek.

In the Littoral Zone adjoining Mattawoman Creek, groundwater begins to rise vertically and eventually discharges to the land surface (**Figure 5-2**). Most of this discharge is concentrated in the intertidal zone, immediately above and below the average water level in the creek (Bokuniewicz, 1992). The long-term average discharge velocity is estimated to be between 0.04 and 0.08 ft/d upward through the Littoral Zone. At low tide, numerous small springs and seeps are evident in the intertidal zone. Discharge rates vary inversely with tide levels, with the highest discharge rate expected to occur during low tides. Groundwater flow reverses during

periods of high tide when water in creek infiltrates a short distance into the Littoral Zone sediment. This cyclic discharge/recharge results in increased mixing of surface water and groundwater in the near-surface Littoral Zone sediments (Westbrook et al., 2005; Robinson et al., 1998). However, chloride concentrations decrease rapidly with depth indicating mixing of surface water and groundwater is limited.

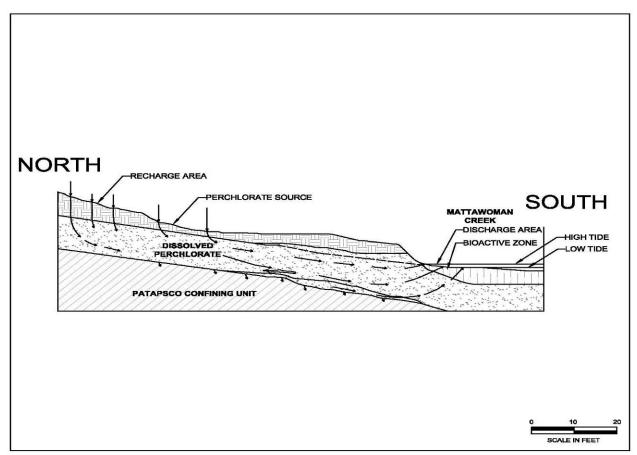


Figure 5-2. Conceptual Model of Perchlorate Transport

The shallow sediments in the Littoral and Subtidal Zones appear as organic rich muck (**Figure 5-3**) due to deposition of plant material occurs in these zones. The TOC in shallow and deep sediment samples from the Littoral Zone averaged 9,800 and 2,400 mg/kg, respectively (**Table C1** in **Appendix C**).



Figure 5-3. Photograph Showing Organic Muck Layer (Eight inches of organic much obtained by plunging an open ended tube into the creek bottom at the edge of the Subtidal Channel and Subtidal Shallows)

A variety of different pollutants can be anaerobically biodegraded in anaerobic wetland sediments. Lorah et al. (1997) and Lorah and Olsen (1999) found evidence of anaerobic biodegradation of chlorinated VOCs as groundwater migrated from an aerobic sand aquifer upward through anaerobic wetland sediments. Tobias et al. (2001) report that anaerobic, organic-rich, marsh sediments often have high potential rates of nitrate reduction. Portnoy et al. (1998) and Nowicki et al. (1999) also describe the potential for high denitrification rates, but caution that in more sandy, tidal estuaries, rapid groundwater flow through seeps may influence the extent of nitrate removal. Conditions favoring nitrate and perchlorate reduction are similar, suggesting the potential for rapid perchlorate degradation in the organic rich, Littoral Zone sediments at the study site.

Field monitoring data indicate that perchlorate rapidly biodegrades under anaerobic conditions as groundwater migrates upward through the organic-rich Littoral Zone sediments before discharging to the surface. Perchlorate was below the method detection limit ($< 1 \,\mu g/L$) in five of six samples collected from shallow monitoring points within the Littoral Zone (TP-1 and TP-4) over the study period. In the one sample above the detection limit ($6.7 \,\mu g/L$ in TP-4 on

3/30/07), perchlorate had been reduced by 99.8% from the value observed 3.5 ft deeper in the aquifer (**Table C2** in **Appendix C**)

In Section 6.0, multiple lines of evidence will be used to evaluate and document the natural attenuation of perchlorate in groundwater in the vicinity of Building 1419, Naval Surface Warfare Center, Indian Head, MD.

6.0 Field MNA Evaluation Program

Acceptance of MNA as a groundwater remedy requires multiple lines of evidence. As discussed in previous sections, analytical methods are available to monitor the concentration of perchlorate in the environment with high sensitivity and selectivity. Geochemical tests can indicate whether ambient conditions are conducive to perchlorate biodegradation, and molecular biological tools are available to monitor the activity and sustainability of perchlorate-reducing bacterial populations. Using these tools and the direction offered in the MNA Protocol, the three tiers of evaluation were applied to the Indian Head site: 1) plume stability and geometry assessment; 2) biogeochemical parameter and biological indicator evaluation; and 3) biodegradation rate estimation (ESTCP, 2008). The following sections summarize our evaluation of the Indian Head site and the lines of evidence supporting the use of MNA as a groundwater remedy.

6.1 Tier 1 Evaluation – Plume Geometry and Stability

6.1.1 Plume Geometry

Historical data can be used effectively to delineate the extent of the contamination and determine the fate of contaminants of concern. With a properly designed monitor well network, trends in the data can successfully illustrate plume geometry and stability. Ideally, the contaminant plume should be stable or retreating. A stable or shrinking perchlorate plume indicates that natural processes are attenuating perchlorate more rapidly than it is released from the source area. Perchlorate concentrations, summarized from the April 2008 performance monitoring event at the Indian Head site, are shown in **Figure 6-1.** The perchlorate plume extends approximately 460 feet from the Building 1419 area to the Subtidal Channel. The groundwater flow net shown as **Figure 4-11** demonstrates that while the perchlorate is present at the southwest extent of the plume, most of the plume discharges to the south with groundwater to the creek. The data generated during the MNA demonstration suggested that plume geometry has changed very little over time.

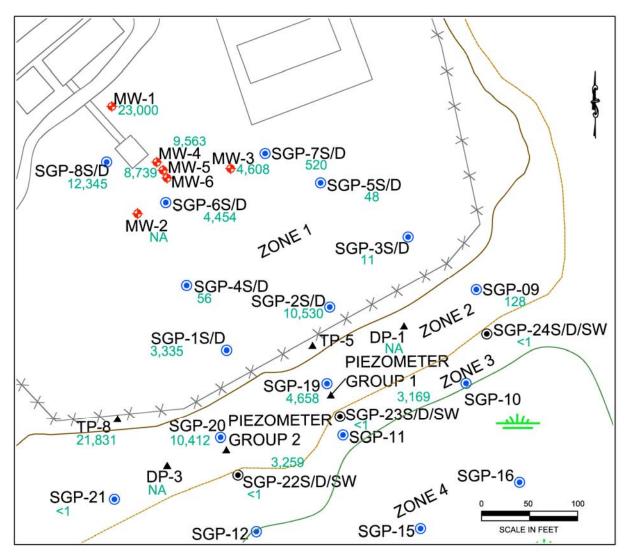


Figure 6-1. Perchlorate Concentration Map (April 2008)

A longitudinal profile through the different biogeochemical zones is presented graphically in **Figure 6-2** including average levels of perchlorate (Perch), chloride (Cl⁻), methane (CH₄) and pH in groundwater/pore water in each zone. Perchlorate concentrations are elevated in the both the shallow (avg. = 5,611 μ g/L) and deep (avg. = 2,792 μ g/L) groundwater on the land and in the deep groundwater beneath the Littoral Zone sediments (avg. = 3,618 μ g/L). The transition occurs within the shallow creek sediment in the Littoral Zone where perchlorate is not detected. The loss of perchlorate is the result of both biodegradation and dilution with surface water. The impact of biogeochemical conditions on perchlorate biodegradation is discussed in Section 6.2.

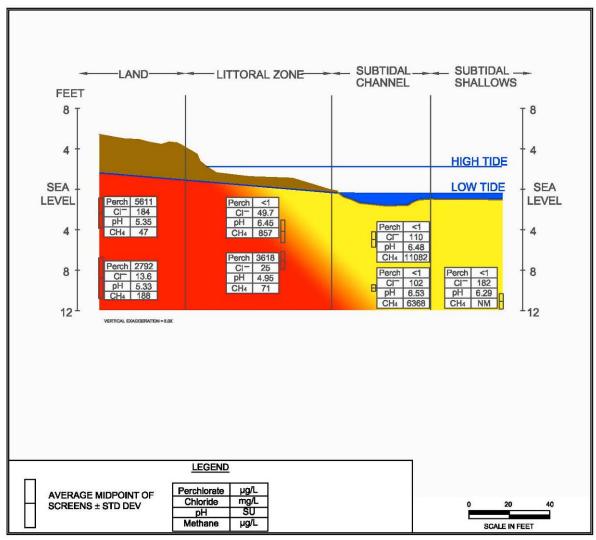


Figure 6-2. Geochemical Changes in Groundwater (on left) and Sediment Pore Water (on right).

6.1.2 Plume Stability

Many regulatory agencies require that contaminant plumes be stable or shrinking before MNA can be employed as the primary groundwater remediation technology. At Indian Head, downgradient migration of perchlorate is limited by the organic rich sediments adjoining Mattawoman Creek (**Tables 6-1a, b**). Seven of deep monitoring points in the Littoral Zone (SGP-9, SGP-19, SGP-20, TP-3, TP-5, TP-7 and TP-8) have elevated concentrations of perchlorate. However, there is no evidence of an increase in concentration over time. Concentrations in all the shallow and intermediate monitoring points (TP-1, TP-2, TP-4, and TP-6) remained low with no indication of an increase with time, indicating perchlorate is not gradually migrating upward through the Littoral Zone. Perchlorate was less than 1 μ g/L in monitoring points within the Subtidal Channel indicating perchlorate was not migrating underneath or into the Subtidal Channel (**Table 6-1c**). No statistically significant trends in concentration versus time were detected for any Littoral Zone or Subtidal Channel well (**Appendix D**).

Table 6-1a Perchlorate Concentrations (µg/L) in Littoral Zone Points								
SGP-9 SGP-19 SGP-20								
June 2006	200	4,400	13,000					
Sept 2006	61	4,200	11,000					
March 2007	NS	3,400	10,000					
August 2007	<1	4,200	1,700					
April 2008	130	4,700	10,412					

	Table 6-1b								
Perchlorate Concentrations (µg/L) in Littoral Zone Piezometer Groups									
	TP-1	TP-2	TP-3	TP-4	TP-5	TP-6	TP-7	TP-8	
March 2007	<1	5.9	2,700	6.7	1800	3.4	3,200	34,000	
August 2007	<1	<1	2,400	<1	1300	<1	640	NS	
April 2008	<4	<1	3,200	<1	1300	<1	3,300	22,000	

NS - Not Sampled

Table 6-1c									
Perchlorate Concentrations (µg/L) in Subtidal Channel Monitoring Points									
	SGP-21 SGP-22S SGP-22D SGP-23S SGP-23D SGP-24S SGP-24I						SGP-24D		
Sept 2006	<1	<1	<1	<1	<1	<1	<1		
August 2007	<1	<1	<1	<1	<1	<1	<1		
April 2008	<1	<1	<1	<1	<1	<1	<1		

6.1.3 Effect of Dilution on Perchlorate Concentrations

The Littoral Zone monitoring data presented in **Table 6-1b** show that perchlorate concentrations decline from a range between 600 to 3400 μ g/L in the deeper monitor points (TP-3 and TP-7) to near the analytical detection limit in the shallow (TP-1 and TP-4) and mid-depth (TP-2 and TP-6) monitoring points. However, some portion of this decline is likely due to dilution with surface water.

One approach for evaluating the relative impact of dilution is to examine changes in chloride concentration with depth. Average chloride concentrations in the deep piezometers are low (11 mg/L in TP-3; 26 mg/L in TP-7) and similar to groundwater near the perchlorate source area (6 to 30 mg/L). In contrast, surface water in the Subtidal Channel had an average chloride concentration of 174 mg/L over the monitoring period. The steady increase in chloride concentration as water flows upward through the Littoral Zone is likely due to tidally driven mixing of surface water and groundwater. By linear interpolation, we can then estimate the relative contribution of groundwater and surface water at each depth. As illustrated in **Table 6-2**, groundwater with an average chloride concentration of 84 mg/L (TP-1) would result from mixing 55% groundwater with 45% surface water. Mixing ratios in TP-2, TP-4 and TP-6 are lower, varying from 79 to 95% groundwater with 21 to 5% surface water.

Table 6-2 Groundwater and Surface Water Mixing Ratios in Piezometer Groups 1 and 2

			%	%				
	Elevation	Average Cl	Ground	Surface	Calculated Cl			
	(ft msl)	(mg/L)	-water	Water	(mg/L)			
Piezometer Group 1								
Surface Water	0	174	0	100	174			
TP-1	-3.2	84	55	45	84			
TP-2	-5.2	45	80	20	45			
TP-3	-6.7	11	100	0	11			
		Piezometer	Group 2					
Surface Water	0	175	0	100	175			
TP-4	-3.2	57	79	21	57			
TP-6	-5.2	33	95	5	33			
TP-7	-6.7	26	100	0	26			

As groundwater migrates upward from TP-3 to TP-2, perchlorate declines by three orders of magnitude. At most, 50% of this decline is due to dilution (see Table 6-2), indicating biodegradation is responsible for over 99% of the decline in perchlorate. The large relative change in perchlorate concentration compared to chloride concentration is illustrated in **Figure 6-3**. Perchlorate and chloride concentrations are plotted on a log scale over a four log unit range so changes in perchlorate and chloride can be visually compared. In Piezometer Group 1, perchlorate declines 1000x as groundwater migrates upward from -6.7 ft (TP-3) to -5.2 ft (TP-2), while chloride only increases by 2x. Similar patterns are observed in Piezometer Group 2 where perchlorate declines 1000x while chloride increases by only few percent. These results demonstrate that perchlorate is attenuated much more rapidly than would be expected based on dilution alone.

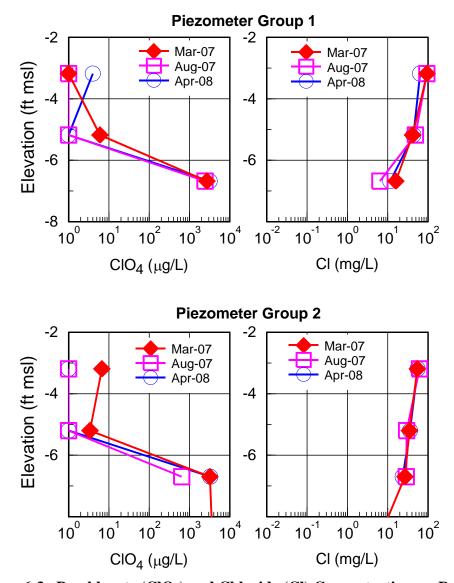


Figure 6-3. Perchlorate (ClO₄) and Chloride (Cl) Concentration vs. Depth in Piezometer Groups 1 and 2

6.1.4 Source Area Attenuation

In contrast to the downgradient wells, many of wells located in the upgradient portion of the plume near the source area have shown significant declines in concentration with time. These declines are likely due to flushing of highly soluble perchlorate out of the aquifer by incoming groundwater.

Attenuation rates in individual wells were calculated by plotting perchlorate concentration versus time and fitting the data to a first-order function $[C_t = C_i \exp(-K_1 t)]$ where C_t is the observed concentration at different times (t), C_i is the fitted initial concentration and K_1 is the estimated 1^{st} -order decay rate. **Figure 6-4** is an example of the 1^{st} -order attenuation curve fit to the data from MW-4, a well that has been monitored for six years. The attenuation rate constants, time to remediation, and 90% confidence intervals are reported in **Appendix D**.

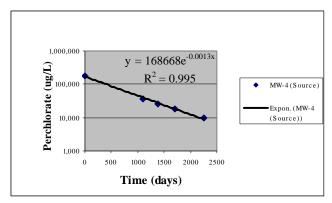


Figure 6-4. Perchlorate Concentration vs. Time Curve Fit for MW-4

Table 6-3 summarizes the attenuation rate constants for three monitoring wells near the source area (MW-1, MW-4, and SGP-6S) where the slope of the regression line was statistically significant at the 90% level (F statistics < 0.10). In all wells with a statistically significant trend, the concentration was declining with time. Estimated time to reach the cleanup standard of 24.5 μ g/L was also calculated using the best fit linear regression and varied from 11 to 27 years.

First-O	Table 6-3 First-Order Concentration vs. Time Attenuation Rates in Zone 1 Wells								
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$									
MW-1	0.32	0.63	0.06	5	27				
MW-4	0.50	0.91	0.003	5	18				
SGP-6S	0.57	0.99	0.04	3	11				

6.1.5 Mass Flux

Mass flux is used to describe the contaminant mass discharge rate in a groundwater plume in units of mass per time passing across a plume transect. Contaminant mass flux estimates were determined using the transect method (Newell et al., 2003). The calculations were performed using *The Mass Flux Toolkit* (Farhat et al., 2006) developed under ESTCP to compare different mass flux approaches, calculate mass flux from transect data, and apply mass flux to manage groundwater plumes. The data input and results are included in **Appendix E.**

Mass flux calculations were based on a 100-foot long segment of the plume located within the evaluation area. This segment transects the western-most of the three groundwater flow tubes as shown in **Figure 4-11**. **Figure 6-5** highlights the location of the transects used in the mass flux evaluation.

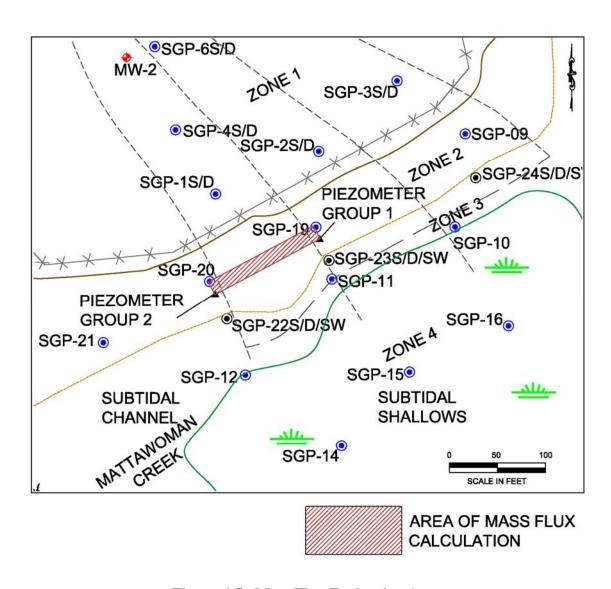


Figure 6-5. Mass Flux Evaluation Area

Four transects were established to analyze groundwater flux. All were oriented approximately normal to the direction of groundwater flow using estimated hydraulic conductivity and average gradients were calculated (transient tidal effects were ignored). **Figure 6-6** shows the location of the four transects in an isometric view. Transect 1 is oriented vertically and is located between wells SGP-19 and SGP-20. Transects 2, 3, and 4 are located between Piezometer Groups 1 and 2. Perchlorate flux calculations for Transect 2 use data from the deeper piezometers TP-3 and TP-7 screened approximately between elevation -6.2 and -7.4 ft msl. Perchlorate flux calculations for Transect 3 use data from intermediate piezometers screened between -4.7 to -5.7 ft msl. Transect 4 is the Littoral Zone creek bottom (mud surface). In evaluating groundwater and perchlorate flux, all of the groundwater entering the Littoral Zone across Transect 1 was assumed to eventually discharge upward across Transect 4 into the creek.

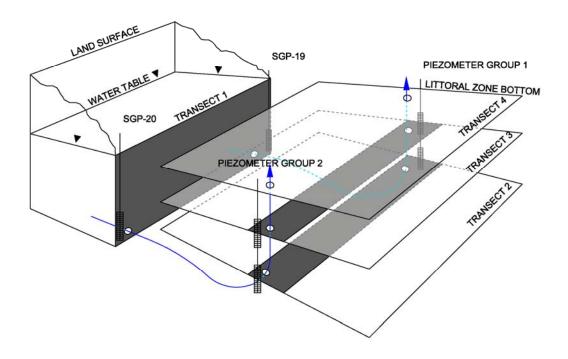


Figure 6-6. Orientation of Mass Flux Transects

At Transect 1, groundwater flow is assumed to be horizontal or nearly horizontal and driven by the general water table gradient of 0.020 ft/ft. Aquifer testing of sediment along the bank in the Littoral Zone indicated an average hydraulic conductivity of 2.3 ft/d. The creek bottom occurs at approximately elevation -0.5 ft msl in this area and the thickness of the surficial aquifer was estimated to be approximately 12 feet. The dimensions of Transect 1 input into the *Mass Flux Toolkit* are 12 feet (vertical) by 100 ft (horizontal) for an area of 1,200 ft².

For Transect 1, the calculated groundwater flux $(Q=K_iA)$ is 55.2 ft³ per day. By continuity, the average discharge rate for groundwater passing through Transect 4, entering the creek is also assumed to be 55.2 ft³ per day with the discharge surface being spread over the distance between the low tide line at the creek bank and the Subtidal Channel, a distance of approximately 50 feet. The dimensions of Transect 4 were input as a length of 50 ft and width of 100 ft, with the width dimension of the transect being oriented parallel to the creek bank. **Table 6-4a** summarizes the groundwater flux calculations.

At Transect 2, the direction of flow is assumed to be upward, but the vector direction is unknown. The hydraulic conductivity was estimated to be approximately 0.4 ft/d (a value selected to be between the estimated vertical K_z of 0.23 ft/d and the horizontal conductivity K_x of 2.3 ft/d). By continuity, the gradient was then calculated to be 0.026 ft/ft.

Transect 3 is also located between piezometers TP-2 and TP-6 and is oriented nearly horizontally. The groundwater transect is 100-feet wide by 50-feet long. From continuity, 55.2 ft³ of groundwater pass through the plane on a daily basis. The hydraulic conductivity was estimated to be 0.3 ft/d and the gradient was calculated to be 0.037 ft /ft.

TABLE 6-4a Groundwater Flux Calculations

Transect Number	1	2	3	4
Orientation of Transect	Vertical	Inclined	Slight	Horizontal
			Incline	
Dimension (ft x ft)	12 x 100	50 x 100	50x100	50 x 100
Gradient (ft/ft)	0.020	*0.026	*0.037	*0.048
Hydraulic Conductivity (ft/d)	2.3	0.4	0.3	0.23
Groundwater Flux (ft ³ /d)	55.2	55.2	55.2	55.2

Notes: *Gradients (i) were calculated using estimated hydraulic conductivity values (K) from Q=KiA, where Q was set at 55.2 ft³/d and the equation was solved for i.

The calculations for perchlorate mass flux through the transects are summarized in **Table 6-4b**. Transect 1 incorporates the April 2008 perchlorate data from SGP-19 (4,658 μ g/L) and SGP-20 (10,418 μ g/L). In calculating the perchlorate flux crossing Transect 1, perchlorate concentrations were assumed to be consistent across height of the transect (the aquifer thickness). This was found to be the case in many of the shallow and deeper wells within the land area. The daily perchlorate flux for Transect 1 was calculated by the *Mass Flux Toolkit* to be 12.4 grams (Appendix E). On a per square foot basis (shaded area in **Figure 6-6**) for Transect 1 (1,200 ft²), this represents a perchlorate flux of approximately 10 mg/day/ft². Dividing this number by the width of the segment (100 ft) parallel to the creek bank suggests that the perchlorate flux entering the sediment beneath the creek is approximately 124 mg per day per linear foot (mg/d/lin ft) of bank.

Transect 2 also incorporates the April 2008 perchlorate data from TP-3 (3,169 μ g/L) and TP-7 (3,259 μ g/L). The perchlorate flux calculation was based on an inclined plane with of 100 feet and an inclined length dimension of 2 feet, for an area of 200 ft² (the shaded area in **Figure 6-6**). The perchlorate mass flux calculated by the *Mass Flux Toolkit* for the 200 ft² area comprising a portion of Transect 2 is 0.208 g/d (Appendix E). This is equivalent to a daily perchlorate flux of 0.001 g/ft²/d, or an average perchlorate daily perchlorate flux of approximately 5.2 mg/d/lin ft of creek bank.

Perchlorate has not been detected in either of the two piezometers used to model Transect 3. However, in order to estimate a perchlorate mass flux, concentrations of the laboratory detection limit $(1.0 \,\mu\text{g/L})$ for perchlorate were input into the analysis for both of the piezometers. The perchlorate mass flux calculated for the 200 ft² portion of Transect 3 is 6.92 x 10^{-5} grams per day (Appendix E). This is equivalent to a daily perchlorate flux of $3.46 \, \text{x} \, 10^{-7} \, \text{g/ft}^2/\text{d}$, or an average perchlorate daily perchlorate flux of approximately $1.73 \, \text{x} \, 10^{-2} \, \text{mg/d/lin}$ ft of creek bank. Perchlorate mass flux was not calculated for Transect 4 as perchlorate concentrations are reduced to non-detectable concentrations in Transect 3.

TABLE 6-4b Perchlorate Mass Flux Calculations

Transect Number	1	2	3	4				
Orientation of Transect	Vertical	Inclined	Slight	Horizontal				
			Incline					
Perchlorate Flux Calculations								
Dimension (ft x ft)	12 x 100	2 x 100	2 x 100	Not Evaluated				
Perchlorate Flux (g/d)	12.4	0.208**	6.92 x 10 ^{-5**}	Non Detect				
Perchlorate Flux (mg/d/lin. ft)	124	5.2	1.73 x 10 ⁻²	Non Detect				

Notes: **Flux calculations shown in Appendix E are based on a 2 x100 ft segment of the 50 x100 ft transect plane.

The data show that perchlorate mass flux is reduced to non-detect over a relatively short vertical distance between the screens for the deep piezometers and the intermediate depth piezometers. Data collected from the shallow piezometers confirm that perchlorate concentrations remain below detection.

6.1.6 Summary of Plume Geometry and Stability Evaluation (Tier 1)

Groundwater monitoring data collected as part of the MNA evaluation indicate the following:

- The perchlorate plume is generally stable and there is no evidence of continuing downgradient migration. Concentrations in the most downgradient wells with detectable perchlorate were stable over the monitoring period. Further downgradient, perchlorate concentrations are close to or below the analytical detection limit.
- ➤ Within the Littoral Zone, perchlorate concentrations decline much more rapidly than would be expected based on dilution alone. This implies that perchlorate biodegradation within the organic rich sediments is the dominant attenuation mechanism.
- > Perchlorate concentrations are gradually declining with time in the source area monitor wells. If current trends continue, perchlorate concentrations will drop below 24.5 μg/L in many of these wells within 30 years.
- > The estimated perchlorate mass flux decreased by over 4 orders of magnitude during migration through the organic rich sediments of the shallow Littoral Zone.

6.2 Tier 2 Evaluation – Biogeochemical Parameters and Biological Indicators

Site-specific biogeochemical and biological information can often provide an important indication of the potential for MNA of perchlorate. The following section describes collection and interpretation of biogeochemical and biological monitoring results from the Indian Head site and how this information was used to evaluate the potential for MNA of perchlorate. The results illustrate the use of a tiered approach for evaluating perchlorate MNA as described in "Natural Attenuation of Perchlorate in Groundwater: Processes, Tools and Monitoring Techniques" (ESTCP, 2008).

Perchlorate can be rapidly biodegraded under anaerobic or low oxygen conditions when an external electron donor is present. Biodegradation will be most rapid in the absence of nitrate since many perchlorate degraders are also denitrifiers (Robertson et al., 2007; Herman and Frankenberger, 1999; Coates et al., 1999). Tan et al. (2004a) showed the presence of nitrate can slow perchlorate enzyme activity as it is a competing electron acceptor, but concluded that

because more than one enzyme is involved in the degradation process, nitrate is not a competitive inhibitor of perchlorate reduction. Tan et al. (2004b) and Tan et al. (2005) concluded that organic substrate availability was the limiting factor under high electron acceptor conditions. As a result, the following conditions are expected to be most favorable for perchlorate biodegradation (ITRC, 2002):

- ➤ Available organic carbon;
- \triangleright ORP between 0 and -100 mV;
- ➤ Low levels of dissolved oxygen and nitrate;
- Elevated levels of dissolved iron and/or methane;
- > pH between 6.5 and 7.5; and
- ➤ Active perchlorate-degrading microbial community.

The key geochemical parameters were evaluated in each well or piezometer sampled during the five performance monitoring events over 38 months between February 2005 and April 2008. The methods used were described in **Section 3.5.1**. Additional parameters included chloride, sulfate, phosphate, nitrite, conductivity, temperature, turbidity, dissolved manganese and dissolved iron.

Tables 6-5 and **6-6** summarize the levels of perchlorate, TOC, ORP, pH, methane and chloride in the monitor wells when most recently sampled. The wells were separated into two groups, shallow and deep, based on the elevation of the well screen. The mid-points of shallow well screens are above -5.9 ft msl (ft above mean sea level). The mid-points of deep well screens are below -6.0 ft msl. The tables also list the relative location of each monitoring point: Zone 1 (Land); Zone 2 (Littoral); Zone 3 (Subtidal Channel); and Zone 4 (Subtidal Shallows).

Table 6-5 **Performance Monitoring in Shallow Wells**

	~	_		c widnitoring i	II SHanow	VVCIIS			
Location &	Screen Mid-	*** 11 **	Sample	D 11	mo c	opp.		3.5.0	
Transect	Point*	Well ID	Date	Perchlorate	TOC	ORP	pН	Methane	Chloride (mg/L)
	(ft msl)			(μg/L)	(mg/L)	(mV)	(SU)	(µg/L)	
Land	-1.17	MW-1	4/17/08	18,000	1.7	127	6.12	7	29
Land	1.22	SGP-7S	4/17/08	520	3.2	44	6.27	<4	2.4
Land	-2.99	MW-2	9/28/06	6	5.1	22	6.73	NA	2.1
Land	-3.25	MW-5	4/17/08	8,800	2.7	48	6.46	6	5.3
Land	-3.36	MW-4	4/17/08	9,600	2.5	101	5.95	92	9.4
Land	-0.40	MW-3	4/17/08	4,100	2.2	89	5.19	<4	5.1
Land	-1.19	SGP-8S	4/17/08	12,000	2.0	163	4.41	250	32
Land	-1.90	TP-8	4/16/08	22,000	2.4	132	3.98	130	28
Land-B	-2.21	SGP-4S	4/17/08	56	2.9	17	6.79	48	1.2
Land	-2.24	SGP-6S	4/17/08	4,500	1.6	89	5.23	16	17
Land	-3.23	SGP-3S	4/15/08	11	1.8	53	4.96	<4	16
Land-C	-3.48	TP-5	4/16/08	1,300	2.5	-31	5.98	150	130
Land-C	-3.58	SGP-2S	4/15/08	11,000	1.1	102	4.39	10	17
Land	-3.46	SGP-7D	4/17/08	390	1.7	152	4.74	17	2.8
Land	0.13	SGP-5S	4/17/08	48	1.1	110	4.44	<4	4.9
Land-B	-5.70	SGP-1S	4/15/08	3,300	1.2	84	4.88	8	3.6
Land	-4.51	SGP-5D	4/17/08	210	1.2	98	4.46	18	11
			Average	5,611	2.1	82	5.35	47	18.4
Littoral-C	-3.18	TP-1	4/16/08	<1	4.9	-59	6.50	2,000	64
Littoral-C	-5.18	TP-2	4/16/08	<1	4.3	4-24	6.39	640	44
Littoral-B	-3.17	TP-4	4/16/08	<1	5.9	-9	6.68	400	56
Littoral-B	-5.17	TP-6	4/16/08	<1	2.4	1.4	6.24	400	36
			Average	<1	4.4	-23	6.45	857	49.7
Channel-B	-3.96	SGP-22S	4/16/08	<1	11.4	-3.9	6.25	4,549	110
Channel-B	-5.38	SGP-22D	4/16/08	<1	4.9	383	3.41	25	97
Channel	-4.81	SGP-24S	4/16/08	<1	11.9	-76	6.54	19,340	130
Channel-C	-5.69	SGP-23S	4/16/08	<1	11.8	-77	6.66	9,356	100
			Average	<1	11.7	-52	6.48	11,082	110

^{*}Shallow wells have screen mid-point starting at -5.90 ft above mean sea level (ft msl) or above. Transects (Sections) are shown on **Figures 4-3 and 4-4.**

Table 6-6 **Performance Monitoring in Deep Wells**

				e Monitoring	s in Deep	VV CIIS			
Location & Transect	Screen Mid- Point*	Well ID	Sample Date	Perchlorate	тос	ORP	рН	Methane	Chloride
	(ft msl)			(μg/L)	(mg/L)	(mV)	(SU)	(μg/L)	(mg/L)
Land	-12.07	SGP-8D	4/17/08	11	4.5	50	6.24	<4	22
Land	-6.09	SGP-6D	4/17/08	<1	24.4	18	6.35	1,098	26
Land-C	-8.19	SGP-2D	4/16/08	10,000	1.2	91	5.05	9	13
Land	-8.14	SGP-4D	4/17/08	2,400	2.0	78	5.47	7	4.1
Land	-8.42	SGP-3D	4/16/08	210	1.0	104	4.01	6	8.7
Land-B	-9.88	SGP-1D	4/16/08	4,000	1.2	86	4.88	7	7.5
			Average	2,792	5.7	71	5.33	188	13.6
Littoral-C	-8.21	SGP-19	4/16/08	4,700	1.2	13	4.89	<4	6.2
Littoral	-8.10	SGP-9	4/16/08	130	0.9	48	4.90	20	18
Littoral-B	-6.30	SGP-20	9/27/06	10,000	1.6	48	4.25	116	14
Littoral	-6.35	SGP-21	4/17/08	<1	8.0	1	6.22	117	95
Littoral-B	-6.67	TP-7	4/16/08	3,300	1.6	52	4.84	25	24
Littoral-B	-9.17	DP-2	3/30/07	3,700	NA	NA	NA	NA	6.2
Littoral-C	-6.85	TP-3	4/16/08	3,200	1.0	45	4.62	147	12
			Average	3,618	2.4	34	4.95	71	25.0
Channel-C	-10.00	SGP- 23D SGP-	4/16/08	<1	4.4	-29	6.70	630	100 100
Channel	-9.53	24D	4/16/08	<1	4.7	-80	6.36	12,105	100
			Average	<1	4.6	-55	6.53	6 ,368	100
Shallows	-11.42	SGP-10	9/26/06	<1	7.4	-57	6.05	NA	16
Shallows-C	-11.11	SGP-11	9/26/06	<1	10.0	-83	5.94	NA	62
Shallows	-10.52	SGP-15	9/26/06	<1	13.0	-96	6.34	NA	240
Shallows	-11.90	SGP-16	9/26/06	<1	13.0	-119	6.42	NA	190
Shallows-B	-10.84	SGP-12	9/26/06	<1	14.0	-226	6.22	NA	190
Shallows	-12.50	SGP-13	9/26/06	<1	14.0	-130	6.40	NA	230
Shallows	-10.55	SGP-14	9/26/06	<1	16.0	-151	6.30	NA	260
Shallows	-10.23	SGP-17	9/26/06	<1	32.0	-139	6.46	NA	180
Shallows	-10.67	SGP-18	9/26/06	<1	35.0	-147	6.47	NA	150
			Average	<1	17.2	-127	6.29	NA	180

^{*}Deep wells have screen mid-point starting at -6.00 ft above msl or deeper Transects (Sections) are shown on **Figures 4-3 and 4-4**

6.2.1 Total (or Dissolved) Organic Carbon

Total or dissolved organic carbon in groundwater serves as an electron donor for perchlorate biodegradation, with TOC levels > 2 mg/L considered to be a favorable indicator of perchlorate biodegradation (ESTCP, 2008). Naturally occurring sources of carbon can be found in wetlands, Littoral Zones, and riparian buffers. Rectanus et al. (2007) showed that aquifer sediments can be the source of organic carbon capable of supporting reductive dechlorination of chloroethene compounds. When perchlorate plumes enter carbon-rich environments, there is increased potential for perchlorate MNA.

Beneath the Land Zone, the TOC of shallow and deep groundwater is typically in the range of 2 mg/L (**Tables 6-5** and **6-6**), with the exception one anomalously high value of 24.4 mg/L TOC observed in SGP-6D. The low TOC levels in the Land Zone are less than optimal for perchlorate biodegradation.

The shallow sediments in the Littoral and Subtidal Zones appear as organic-rich muck (**Figure 5-3**). In sediment samples collected during monitor well installation in June 2006, average TOC levels were 9,800 and 2,370 mg/kg in shallow and deep sediment, respectively (**Table C1** in **Appendix C**). Moving away from the shoreline, the TOC in shallow and deeper sediments beneath the Subtidal Shallows averaged 30,700 and 34,400 mg/kg, respectively.

The high sediment TOC results in an increase in groundwater TOC during migration from the land into the Littoral Zone sediments and Subtidal Channel. **Figure 6-7** shows that TOC concentration in groundwater and pore water increases along transects B-B' and C-C' from the land through the Littoral Zone to the Subtidal Channel and Subtidal Shallows. The results are similar in between the two transects. The somewhat higher TOC levels in the shallow sediments (2.4 to 5.3 mg/L) of the Littoral Zone are likely due to deposition and decay of plant material in this area. The largest TOC increases occur at the transition from the Littoral Zone to the Subtidal Channel. TOC concentrations in the shallow groundwater (pore water) beneath the Subtidal Channel range from 4.9 to 11.9 mg/L and in the deep groundwater from 4.4 to 4.7 mg/L. Further increases are noted beneath the Subtidal Shallows. These elevated TOC concentrations would be expected to support rapid biodegradation of any perchlorate that might reach these zones.

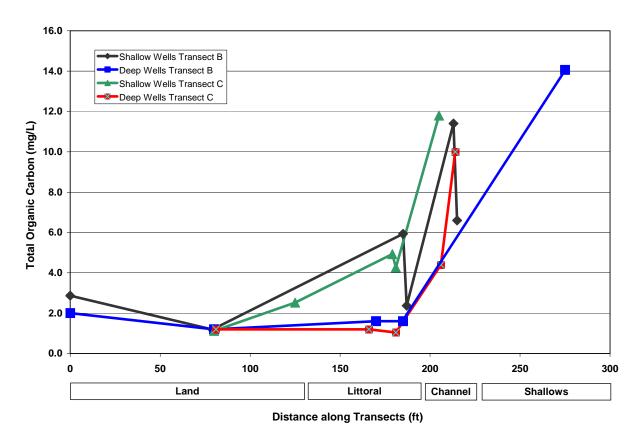


Figure 6-7. Changes in Total Organic Carbon along Transects B-B' and C-C'

6.2.2 Oxidation-Reduction Potential

ORP is a measure of the relative oxidizing or reducing condition of an aquifer. The ORP of groundwater generally ranges from -400 mV to +800 mV. As illustrated in **Figure 6-8**, perchlorate reduction typically begins when ORP drops below about 0 mV (ITRC, 2002). In most cases, the ORP will not drop below -100 mV until all the perchlorate has been consumed.

Tables 6-5 and **6-6** show the ORP measurements in shallow and deep groundwater in the monitoring network mostly from data collected in April 2008. Some additional dates are used to provide a more comprehensive overview of the data. **Figure 6-9** shows ORP values in transects B-B' and C-C'' relative to distance from the shoreline. In the Littoral Zone, ORP is appropriate for perchlorate biodegradation, and then decreases further in the Subtidal Channel and Shallows once all the perchlorate has been depleted. The ORP in the shallow mainland aquifer is generally oxidative ranging from +17 and +102 mV. Pore water within the creek sediment becomes progressively more reducing with increasing distance from the shore; shallow and deep Littoral Zone (-23 and +34 mV, respectively), shallow and deep Subtidal Channel (-52 and -55 mV, respectively); and deep Subtidal Shallows (-127 mV). Decreasing ORP is correlated with increasing TOC ($r^2 = 0.71$).

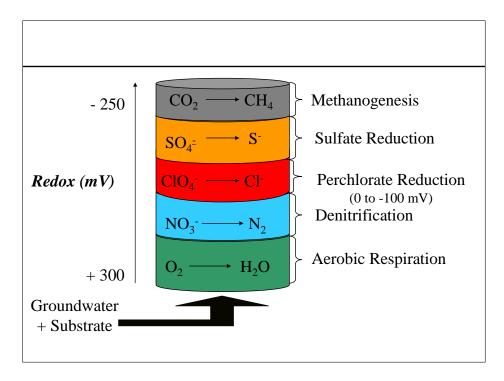


Figure 6-8. Oxidation-Reduction (Redox) Potential for Degradation Processes (ITRC, 2002)

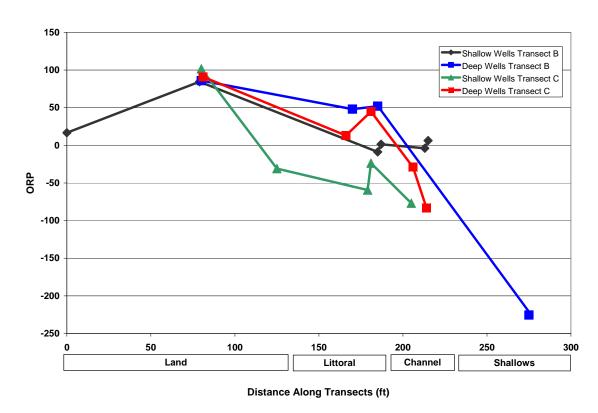


Figure 6-9. Changes in Oxidation-Reduction Potential along Transects B-B' and C-C'

6.2.3 Dissolved Oxygen

Perchlorate reduction can be inhibited in some organisms when dissolved oxygen levels exceed 2 mg/L (Coates and Achenbach, 2006; Chaudhuri et al., 2002). So in theory, the presence or absence of dissolved oxygen should be an important indicator of the potential for perchlorate reduction. However in practice, measured dissolved oxygen levels may not be reliable.

Groundwater samples were collected from each well by low flow sampling using a peristaltic pump. Once pH, temperature and conductivity levels stabilized, DO was measured by inserting a CHEMetricsTM high DO ampoule (1.0-12 mg/L range) into the end of the plastic tubing as water flowed out. The end of the ampoule was then snapped off, the ampoule mixed, and color change was visually observed to determine oxygen content. When the oxygen concentration was less than 1.0 mg/L, the process was repeated with the low DO range (0.1 mg/L to 1.0 mg/L) ampoules. By inserting the end of the ampoule into the flowing water stream, we had hoped to prevent introduction of atmospheric oxygen into the sample. Unfortunately, this approach does not appear to have been fully effective. Field measurements of dissolved oxygen (DO) concentrations measured in wells during this project are presented in **Table C3** in **Appendix C.**

As described below, wells installed in the Subtidal Channel and Shallows had elevated levels of dissolved iron and methane, indicative of strongly reducing anaerobic conditions. Yet substantial amounts of dissolved oxygen (2 to 5 mg/L) were occasionally observed in these wells. These observations are contradictory since iron reduction and methanogenesis would be strongly inhibited at these DO levels.

Table 6-7 shows measured values of DO, iron and methane in SGP-22D, -23D and -24D on three different dates. In all three wells on every date, measured DO levels were 0.8 mg/L or greater. If oxygen were actually present in the groundwater at these levels, iron reduction and methanogenesis would be completely inhibited. It seems likely that there was some error in the DO measurements. Potential sources of error include: (a) introduction of oxygen to the aquifer as a result of well installation just prior to sampling on September 27, 2006 and (b) introduction of oxygen to the wells by purging the wells dry before allowing recharge and sampling.

Table 6-7 Comparison of DO, Iron and Methane Levels in SGP-22D, -23D and -24D

Monitoring Point	Date	Dissolved Oxygen (mg/L)	Iron (mg/L)	Methane (mg/L)
SGP-22D	9/27/06	4.5	390	NA
	8/8/07	1.5	>300	0.012
	4/16/08	1.0	175	0.025
	9/27/06	5.0	30	NA
SGP-23D	8/8/07	3.5	>300	1.2
	4/16/08	0.8	45	0.63
SGP-24D	9/27/06	2.5	10	NA
	8/8/07	2.0	300	4.4
	4/16/08	0.8	5	12. / 11.

Monitoring data collected during this study suggest that field measurements of dissolved oxygen obtained using low-flow purging techniques may not provide a reliable indicator of *in situ* redox conditions and the potential for perchlorate reduction.

6.2.4 Nitrate

Many DPRBs can reduce nitrate as well as perchlorate (Herman and Frankenberger, 1998) and perchlorate reduction and denitrification (the conversion of nitrate to nitrogen gas) require similar geochemical conditions. Nzengung et al. (2008) observed that indicators of nitrate reduction should also be good indicators of perchlorate reduction. However, high levels of nitrate can inhibit perchlorate reduction (Chaudhuri et al., 2002; Krauter et al., 2005). As a result, low nitrate levels (< 5 mg/L) are preferred for the most efficient perchlorate attenuation. However, the presence of nitrate does not preclude perchlorate reduction since some species of DPRB will degrade perchlorate in the presence of nitrate (Coates and Achenbach, 2006).

In upgradient wells near the source area (MW-1, MW-5, SPG-4S, SPG-8S), nitrate levels are elevated, presumably due to oxidation of ammonia associated with ammonium perchlorate. However, as groundwater migrates downgradient, nitrate levels decline suggesting some biological reduction in occurring. As groundwater enters the Littoral Zone, nitrate levels drop below 5 mg/L and then drop below the analytical detection limit (0.5 mg/L) indicating good conditions for perchlorate reduction.

6.2.5 Iron

An increase in dissolved iron, Fe(II), can be an indicator of a reducing environment conducive to perchlorate degradation. Dissolved iron concentrations greater than 0.5 mg/L suggest conditions favorable for perchlorate biodegradation.

Fe(II) was measured frequently during the performance monitoring using Chemetrics[®] field test kits. The colorimetric test is semi-quantitative and can be influenced by natural coloration of the water sample. The results of analysis of groundwater collected from wells and piezometers in shallow and deep groundwater along transects B-B' and C-C' are shown in **Table 6-8.**

The increase in Fe(II) and methane concentrations generally follow the decrease in ORP as discussed in previous sections. Fe(II) concentrations in the sediment pore water generally increases with increasing distance south from the creek bank. Fe(II) concentrations are consistently highest in pore water collected from sediment in the Subtidal Channel and Subtidal Shallows, likely a result of being more strongly reducing in these environments that are continuously submerged. There is no distinguishable difference between Fe(II) concentrations measured in shallow or deep wells at any similar location.

	Table 6-8								
Dis	Dissolved Iron Concentrations in Shallow and Deep Groundwater								
Location	Sample	Well ID	Dissolved	Sample	Dissolved Iron				
	Date		Iron (mg/L)	Date		(mg/L)			
		Shallow	v Groundwate	er					
Transect B-B' Transect C-C'									
Land	4/15/08	SGP-1S	0	4/15/08	SGP-2S	0			
Land	4/16/08	TP-8	30	4/16/08	TP-5	20			
Littoral	4/16/08	TP-4	7.5	4/16/08	TP-1	5			
Littoral	4/16/08	TP-6	5.0	4/16/08	TP-2	15			
Channel	4/16/08	SGP-22S	45	4/16/08	SGP-23S	90			
Channel	9/27/06	SGP-22D	175						
		Deep	Groundwater						
		Transect B-B'			Transect C-	C'			
Land	4/16/08	SGP-1D	5	4/16/08	SGP-2D	0			
Littoral	9/27/06	SGP-20	5	4/16/08	SGP-19	5			
Littoral	4/16/08	TP-7	15	4/16/08	TP-3	7.5			
Channel				4/16/08	SGP-23D	45			
Shallows	9/26/06	SGP-12	0	9/26/06	SGP-11	120			

6.2.6 Methane

The presence of methane in groundwater is not a prerequisite for perchlorate biodegradation, since methanogenesis requires much more reducing conditions than perchlorate reduction. However, elevated methane levels do indicate the strongly reducing conditions with elevated levels of bioavailable carbon which would result in rapid perchlorate biodegradation.

Tables 6-5 and **6-6** show methane concentrations in the shallow and deep groundwater beneath the site. Methane concentrations are low throughout the source area. However, methane is occasionally detected in upgradient wells (MW-4, SGP-8S/D) suggesting some potential for perchlorate degradation in the Land area. As groundwater enters the shallow Littoral zone sediments, methane concentrations increase appreciably due to increased TOC, lower ORP and neutral pH. The highest methane concentration is reported in pore water within the shallow Subtidal Channel sediment.

6.2.7 pH

The pH in groundwater at the Indian Head site is generally acidic and ranges from 4 to 6 standard units. Perchlorate-reducing bacteria generally grow best at pH values near neutral. However, field studies have shown that some species are capable of growth and perchlorate respiration at pH values as low as 5 (Coates and Achenbach, 2004; 2006). In evaluating the potential for MNA of perchlorate, pH values between 5 and 8 are preferable.

Figure 6-10 shows is pH isocontours obtained from the monitoring network of deeper wells and piezometers in April 2008. There appears to be an area in the south-southeast portion of the site that is with generally more acidic pH. Historical records indicate this area of the site was previously used to off-load acid from a rail spur. Anecdotal information from site managers suggested that historical spills might have occurred in this area although none appear to be documented. The zone of lower pH extends to the south to the vicinity of SGP-22 located at the edge of the Littoral Zone and the Subtidal Channel.

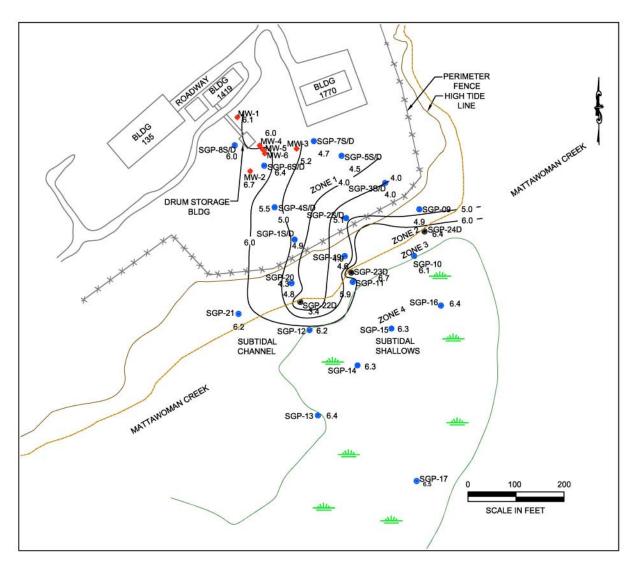


Figure 6-10 Map of pH Concentrations in Deep Groundwater/Pore Water beneath the Site

The average pH of Mattawoman Creek is close to 7.0 (neutral), while the average pH of the shallow and deep portions of the surficial aquifer beneath the Land Zone are pH 5.35 and 5.33, respectively (**Tables 6-5** and **6-6**). The average pH in the deeper pore water beneath the Littoral Zone is pH 4.95, suggesting that this water is primarily groundwater from the land, with little influence of surface water mixing. Conversely, the average pH in pore water within the shallow Littoral Zone sediment is pH 6.45, which more closely resembles surface water.

6.2.8 Temperature

Temperature controls the bacterial metabolic activity. Microbial respiration rates are commonly assumed to roughly double for every 10°C increase in temperature over the temperature range between 5 and 25°C. This general rule is expected to apply to species capable of reducing perchlorate in the environment. Depending on season, there is an 8 to 10°C variation in temperature in the sediment in the Littoral Zone. **Table 6-9** shows the water temperatures and corresponding perchlorate concentrations measured in August 2007 (summer temperatures)

compared to measurements in April 2008 (still winter temperatures) for the piezometers in Piezometer Groups 1 and 2. Biological activity is expected to be greater during the summer months when the groundwater is the warmest. Perchlorate was below detection in the upper and middle piezometers in each group, but the deepest piezometers in each group contained lower concentrations in the warmer groundwater in August than in corresponding cooler groundwater from April.

	Table 6-9 Seasonal Groundwater Temperature Comparison									
	Transec	t B-B'			Transo	ect C-C'				
Piezometer Group 2	Date	Temp(°C)	Perchlorate (µg/L)	Piezometer Group 1	Date	Temp(°C)	Perchlorate (µg/L)			
TP-4	8/9/07	24.9	<1	TP-1	8/9/07	28.2	<1			
11-4	4/16/08	16.5	<1	11-1	4/16/08	16.3	<4			
TP-6	8/9/07	23.8	<1	TP-2	8/9/07	25.6	<1			
11-0	4/16/08	15.3	<1	1P-Z	4/16/08	15.8	<1			
TD 7	8/9/07	25.5	639	TP-3	8/9/07	25.9	2,417			
TP-7	4/16/08	15.5	3,259	117-3	4/16/08	16.7	3,169			

6.2.9 Chloride, Chlorate and Chlorite

If starting chloride concentrations are low and perchlorate is high, increased levels of chloride can provide a direct indication of perchlorate biodegradation. However at the Indian Head site, chloride concentrations were primarily controlled by mixing with brackish water in Mattawoman Creek. Under these conditions, chloride concentrations were not a reliable indicator of the presence or absence of perchlorate biodegradation.

The biodegradation of perchlorate occurs through sequential, enzymatic removal of oxygen atoms from the perchlorate anion. As shown in **Figure 1-1**, the intermediate breakdown products are chlorate (ClO_3^-) and chlorite (ClO_2^-), leading to the formation of chloride and oxygen. EPA Method 300.1 (Rev 1.0) is an ion chromatography method approved for testing chlorate and chlorite in drinking water. A modification of this ion chromatography method was employed at the NCSU CCEE laboratory to analyze for anions including chlorate and chlorite. The detection limit was 0.5 μ g/L. No chlorate or chlorite was reported during any of the sampling events in any of the wells.

The rate controlling step in the biodegradation process is the reduction of perchlorate to chlorate by a perchlorate-reductase enzyme. Chlorate reducers are up to 50 times more abundant than perchlorate reducers, so once formed, chlorate is readily converted to chlorite at rates up to three times faster than the initial step. Chlorite formation could be problematic as it is toxic to bacteria, but the CD enzyme that catalyzes the disproportionation of chlorite to O_2 and Cl^- is the fastest acting enzyme in the sequence. Therefore, no intermediates ordinarily accumulate in solution during perchlorate biodegradation (Magnus XC, 2005; Logan et al., 2001). Thus, like chloride, these intermediates may only be useful indicators when very high concentrations are being degraded, leaving sufficient time for residual concentrations to accumulate.

6.2.10 Microbial Populations

Monitoring of microbial populations and their spatial distributions can provide important evidence about contaminant biodegradation. The Perchlorate MNA Protocol (ESTCP, 2008) describes several methods for enumeration of perchlorate-reducing bacteria including anaerobic

plate counts, most probable number enumeration, and molecular biology tools (MBTs). Several different types of MBTs were used to monitor the activity and spatial distribution of perchlorate reducing bacteria at the Indian Head site.

A wide diversity of microorganisms can degrade perchlorate to chloride and oxygen (Coates et al., 1999; Coates and Pollock, 2003). The perchlorate biodegradation pathways are well understood and the microorganisms involved in perchlorate biodegradation are known to use a variety of different organic substrates as electron donors (Nzengung, 2008) including simple organic acids and alcohols, aromatic hydrocarbons, hexoses, reduced humic substances, both soluble and insoluble ferrous iron and hydrogen sulfide (Coates and Achenbach, 2006). DRPB are widespread in the environment (Coates et al., 1999; Logan, 2001) and bioaugmentation is not usually required to stimulate perchlorate reduction (Coates and Achenbach, 2006). The metabolic versatility of these organisms allows many to function as strict or facultative anaerobes and survive and degrade perchlorate even in microaerophilic environments or environments with low levels of other competing electron acceptors.

As noted during the pre-demonstration testing (Section 3.2.3), DNA-based PCR assays were used initially at the Indian Head site to qualitatively monitor for organisms with the genetic capability to biodegrade perchlorate. The PCR assay used during site screening targeted the chlorite dismutase gene (*cld*) which codes for the CD enzyme. The CD enzyme mediates dismutation of chlorite, the final step in reduction of perchlorate to chloride and oxygen (Gunawan, 2007). During site screening, groundwater was collected from monitoring wells MW-2 and MW-4, which are land wells located near the source, and tested for the presence of the *cld* genes. Groundwater from MW-2 was reported as "+++", a relatively high positive result indicating the presence of the *cld* genes, while the groundwater collected from MW-4 was reported as "+/-" suggesting mixed results (ESTCP, 2007).

As part of the Tier 2 evaluation, the CD enzyme assay was again applied as a screening tool. In August 2007, groundwater samples were collected from 20 monitoring wells/piezometers at the site and shipped to Microbial Insights to be screened qualitatively for the CD enzyme. Sixteen out of 20 samples were reported as strongly positive ("+++") with no distinguishable pattern corresponding to location across the site. After conducting their analyses, Microbial Insights sent the samples to the Soil Microbial Ecology Laboratory at the University of California at Davis under the direction of Dr. Kate Scow where the qPCR assay was used to estimate populations of perchlorate-degrading microorganisms in the samples. The DNA-based qPCR assay was performed on each of the samples targeting the *pcrA* gene which is one of the gene subunits that codes for the perchlorate-reductase enzyme known to mediate the initial breakdown of perchlorate to chlorate and chlorite.

The number of *pcrA* gene copies per mL of groundwater is compared with perchlorate concentrations in the different monitor wells in **Figure 6-11.** The wells are generally arranged with Land Zone wells first, followed by Littoral Zone wells, and Subtidal Channel wells. No samples were collected from any of the wells in the Subtidal Shallows. There is an obvious negative relationship between *pcrA* copies and perchlorate concentrations. In the land wells (SGP-2S, SGP-3S, TP-5, SGP-3D), perchlorate is elevated and *pcrA* copies are below detection (<10 copies/mL). In the shallow wells of the organic-rich Littoral Zone (TP-1, TP-2, TP-4, TP-6), pcrA numbers are high resulting in complete depletion of perchlorate (< 1 µg/L). However in the deeper Littoral Zone wells (TP-3, TP-7, SGP-19, SGP-20, SGP-21), organic carbon levels are

low resulting in much lower *pcrA* numbers and high perchlorate concentrations. This same pattern persists in the subtidal channel (SGP-22S, SGP-22D, SGP-24S, SGP-23D, SGP-24D) where *pcrA* numbers are elevated and perchlorate is below detection.

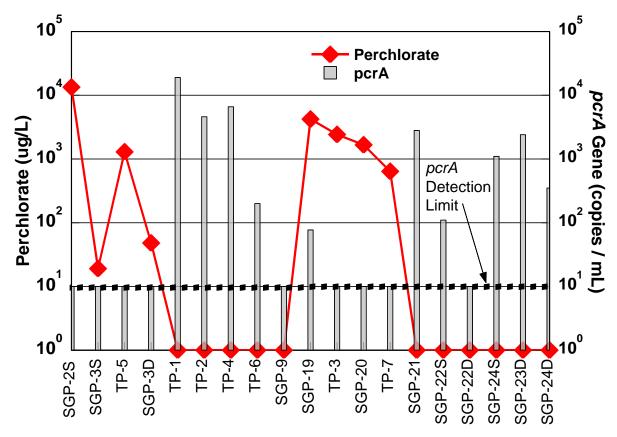


Figure 6-11. Perchlorate Concentration and *pcrA* Gene Copies in Monitor Wells in August **2008.** (Monitor Wells/Piezometers arranged from land installations on left to Subtidal Channel installations on the right. Detection limit for the *pcrA* gene is 10 gene copies/mL; bars below 10 copies/mL included to show sample BDL)

The presence / absence relationship between perchlorate and the pcrA gene is illustrated in **Figure 6-12**. With the exception of one sample (SGP-19, $ClO_4 = 4,200 \mu g/L$, pcrA = 77 copies/mL), whenever the pcrA gene is present above the analytical detection limit, perchlorate is BDL. The very strong relationship between pcrA levels and perchlorate depletion suggests that pcrA levels might be used to identify appropriate conditions for perchlorate attenuation.

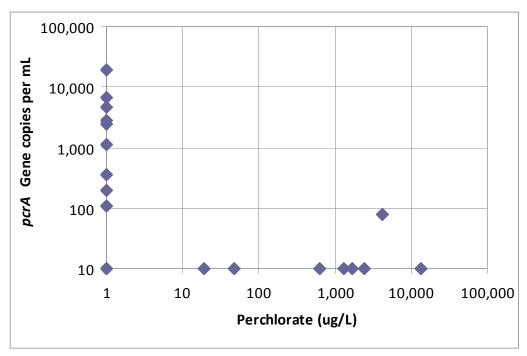


Figure 6-12. Relationship between Perchlorate Concentration and pcrA Gene Copies

Figure 6-13 shows several comparisons between pcrA gene copies, ORP and pH levels in monitor wells within the Littoral Zone and Subtidal Channel in August 2008. pcrA levels are elevated in the range of +50 mV to -100 mV suggesting significant perchlorate degradation may still occur under slightly positive ORP levels. pcrA levels are also elevated in the pH range of 6.0 to 6.5. The higher pcrA levels above pH 6 could imply that more neutral pH values are required for growth of perchlorate degraders. However, the apparent correlation between pH and pcrA levels could also result from the strong correlation between pH and ORP. At lower ORP levels, iron is reduced releasing OH $^-$ with an associated increase in pH. Regardless of the cause, perchlorate degraders can grow to high levels when pH > 6 and ORP is between 0 and +50 mV.

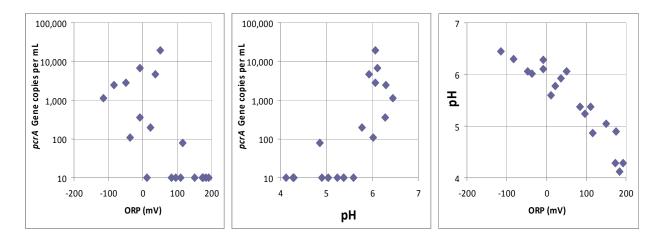


Figure 6-13. Relationships between *pcrA* Gene Copies, ORP and pH in Monitor Wells in August 2008

6.2.11 Summary of Biogeochemical Evaluation (Tier 2)

The biogeochemical evaluation showed that conditions in the land wells could be expected to limit or inhibit perchlorate biodegradation. In contrast, biogeochemical conditions in the shallow Littoral Zone wells are excellent for perchlorate biodegradation.

- ➤ In the land wells, TOC levels were low and probably limited perchlorate biodegradation. However in the shallow Littoral Zone, TOC increases to 2.4 to 5.3 mg/L which should enhance perchlorate biodegradation.
- ➤ In the land wells, ORP levels typically exceed +50 mV, which probably inhibits perchlorate biodegradation. In the Littoral Zone, ORP levels drop enhancing the potential for perchlorate reduction.
- ➤ Nitrate levels are elevated in some source area wells, presumably due to oxidation of ammonium perchlorate. Nitrate levels decline gradually in the land portion of the aquifer indicating some biological reduction potential. Once groundwater enters the shallow Littoral Zone sediments, nitrate declines below the analytical detection limit and perchlorate is depleted.
- Dissolved iron and methane levels are low in most source area wells. However, methane and/or iron are occasionally detected in some land wells suggesting some potential for nitrate and/or perchlorate reduction in the land area. Within the Littoral Zone, elevated levels of dissolved iron and methane are more common indicating more reducing conditions with greater potential for perchlorate biodegradation.
- ➤ In much of the aquifer, pH is below optimum for perchlorate reduction. Monitoring of perchlorate reducing populations shows numbers are elevated in the Littoral Zone where the pH increases to near 6 or above.
- > During winter months, perchlorate degradation rates may slow due to lower temperatures.
- There is a very strong relationship between perchlorate concentrations in the Littoral Zone and the presence of organisms with the pcrA gene which codes for the perchlorate-reductase enzyme. Perchlorate was reduced to below detectable levels in every sample with greater than $10^2 pcrA$ copies/mL (> $10^5 pcrA$ /L). This

relationship can be very useful in identifying conditions for rapid perchlorate biodegradation.

6.3 Tier 3 Evaluation – Biodegradation Rates

In Tier 1, perchlorate concentrations in groundwater were monitored over several years and demonstrated plume stability, a gradual decline in source area concentrations with time, and a decline in contaminant mass with distance downgradient from the source. In Tier 2, data on geochemical conditions in the aquifer and microbial populations demonstrated that biogeochemical conditions were appropriate for perchlorate biodegradation. In Tier 3, laboratory and field measurements were used to estimate biodegradation rates.

There are a variety of approaches for measuring perchlorate biodegradation and estimating rates including laboratory incubations, *in situ* field experiments, and monitoring changes in stable isotope composition. In this project, two different sets of laboratory incubations were run that provided direct evidence of perchlorate biodegradation. A novel *in situ* column experiment was conducted to measure biodegradation rates under field conditions. Unfortunately, physical constraints prevented collection of sufficient perchlorate mass to measure changes in isotopic composition during biodegradation in the Littoral Zone at Indian Head (Section 3.6.3). The following sections illustrate the utility of laboratory incubations and *in situ* columns for estimating perchlorate biodegradation rates and their use in evaluating MNA as a groundwater remedy.

6.3.1 Macrocosm Study

A preliminary microcosm study was conducted during the initial site screening to evaluate the potential for natural attenuation of perchlorate at the Indian Head site. Microcosms were constructed with sediment and groundwater from MW-2 in 245-mL serum bottles and incubated for one year. Perchlorate degraded in these incubations with an estimated first-order decay rate of 0.017 per day (ESTCP, 2007).

Much larger volume macrocosms were constructed and monitored as part of the MNA evaluation presented in this report to: (a) estimate biodegradation rates in sediment from the Littoral Zone at Indian Head; and (b) estimate an isotopic fractionation factor (α) that would be representative of the Indian Head site. The site specific value of α would then be used to interpret changes in isotopic composition observed in monitor wells. Five replicate macrocosms were constructed in 5-gallon carboys with 8 kg of Littoral Zone sediment and filled with groundwater from SGP-2D. The large volume of replicate macrocosms was required to generate enough perchlorate for isotopic analysis. However during the course of the project, it became apparent that the isotopic composition of the Littoral Zone groundwater could not be reliably sampled. As a result, isotopic monitoring of the macrocosms was eliminated. However, traditional monitoring for perchlorate and nitrate continued to estimate degradation rates in the Littoral Zone sediment. Additional details on the macrocosm construction, monitoring and analytical results are presented in Section 3.6.2 and **Appendix F**.

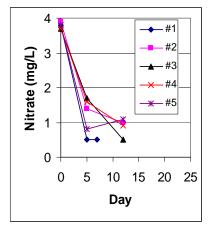
The nitrate and perchlorate sample results for each of the five replicate macrocosms are shown in **Figure 6-14**. All five replicates exhibited the same general behavior. During the first 5 days, perchlorate degradation was slow while nitrate was being consumed. Once nitrate was reduced to roughly 1 mg/L, the perchlorate biodegradation rate increased. Given the apparent relationship

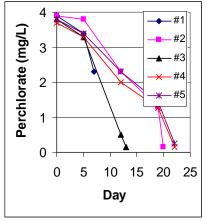
between nitrate and perchlorate degradation, the total electron acceptor concentration was calculated as

Electron Acceptors (meq/L) = $5[NO_3] + 8[ClO_4]$

Where: $[NO_3^-]$ and $[ClO_4^-]$ are in units of millimoles per liter.

Perchlorate in Macrocosms #1 and #3 degraded faster than the other three showing there is some variability in the data. By plotting the sum of nitrate and perchlorate together, the apparent lag in biodegradation (for perchlorate) is eliminated.





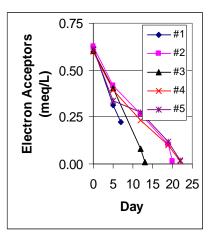


Figure 6-14. Nitrate, Perchlorate, and Electron Acceptor Concentrations vs. Time in Five Replicate Macrocosms Constructed with Littoral Zone Sediment (#1 - #5 indicate replicate number)

Degradation rates were estimated by pooling data from all replicates together for analysis. Zeroorder rates were estimated by regressing measured concentration versus time. First-order rates were estimated by regressing the natural log transform (Ln) of concentration versus time. Estimated zero- and first-order degradation rates for nitrate, perchlorate and total electron acceptors are shown in **Table 6-10** along with the standard error of the estimated rate, correlation coefficients (R²) and statistical significance (p-value). Each of the regressions is plotted in **Figure 6-15** for comparison.

Zero- and first-order degradation rates for nitrate and perchlorate were similar, consistent with the hypothesis that the same biogeochemical processes were controlling the degradation rate. Correlation coefficients and probability of significance were slightly higher for the zero-order regressions and the total electron acceptor concentration. However, there is a high confidence that all the regressions are significant.

Table-10
Nitrate, Perchlorate, and Electron Acceptor Degradation Rates in Littoral Zone Macrocosms

in Dittoral Bone Water Cooping						
Compound Nitrate (mg/L)		Perchlorate (mg/L)	Electron Acceptors (meq/L)			
Linear Regression						
Zero-Order Rate*	0.24 mg/L/d ±0.05	$0.17 \text{ mg/L/d} \pm 0.02$	$0.026 \text{ meq/L/d} \pm 0.002$			
Correlation Coef. (R ²)	0.69	0.83	0.87			
P-Value	1 x 10 ⁻⁴	4 x 10 ⁻⁹	3 x 10 ⁻¹⁰			
Ln Transformed Regression						
First-Order Rate*	$0.13 / d \pm 0.03$	$0.12 / d \pm 0.02$	$0.15 / d \pm 0.02$			
Correlation Coef. (R ²)	0.60	0.61	0.70			
P-Value	7 x 10 ⁻⁴	2×10^{-5}	1 x 10 ⁻⁶			

^{* ±} value is standard error of estimate

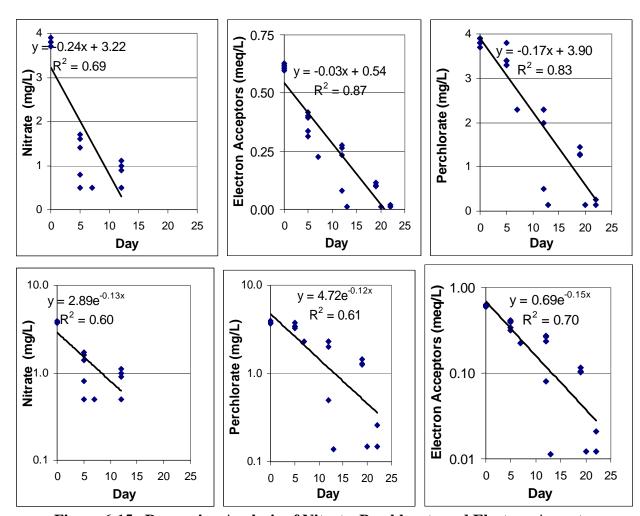


Figure 6-15. Regression Analysis of Nitrate, Perchlorate and Electron Acceptor Concentration vs. Time

Degradation rates in the macrocosms constructed with organic rich Littoral zone sediment were roughly an order of magnitude higher than degradation rates observed in the small microcosm experiments constructed with low carbon sediment and groundwater from MW-2.

6.3.2 In Situ Column Biodegradation (IC) Study

An *in situ* column (IC) study was conducted at Indian Head to estimate the perchlorate biodegradation rate under representative field conditions. The *in situ* columns were installed in the Littoral Zone at Indian Head because prior monitoring data had shown that perchlorate degradation was most rapid and populations of perchlorate degrading bacteria were highest in this area. The column design employed at the Indian Head site was described in Section 3.6.1. Solutions-IES installed ICs near Piezometer Groups 1 and 2 (**Figure 6-16**). The ICs were situated immediately adjacent to the piezometer clusters so that actual perchlorate concentrations at different depths measured in the piezometers could be extrapolated to the conditions within the ICs.

The columns were installed as shallow and deep pairs. The columns were constructed to allow flow through the columns, but to minimize surface water infiltration during testing. However, during initial testing, surface water appeared to be leaking into the shallow ICs at both locations (IC-2 and IC-4), so additional testing utilizing these columns was halted. The biodegradation study continued using only the deeper columns, IC-1 and IC-3, to collect data. The columns were initially operated under the ambient hydraulic gradient which should have resulted in a hydraulic residence time (HRT) within the ICs of roughly 3 to 4-months. However, with this long HRT, perchlorate was never detected in the column effluent. To provide more accurate estimates of the *in situ* biodegradation rates, Solutions-IES shortened the hydraulic residence time by pumping the IC to induce more rapid flow. Biodegradation rates were then estimated using the reduced HRT.

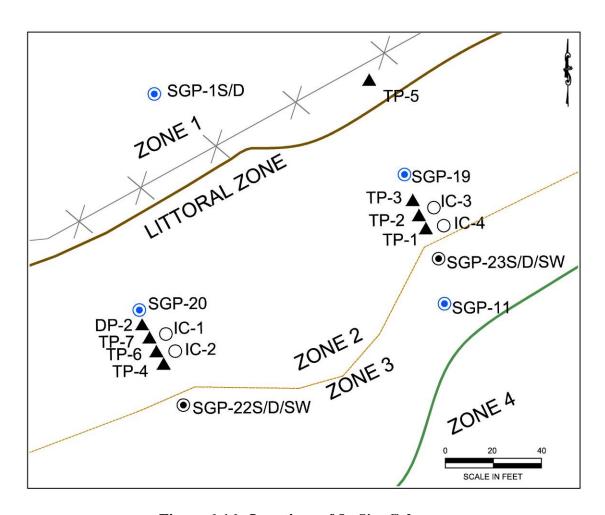


Figure 6-16. Locations of *In Situ* Columns

To perform the test, IC-1 and IC-3 were purged dry and sampled after recharging. The groundwater samples were analyzed for perchlorate, chlorate, chlorite, chloride, bromide, nitrate, nitrite, phosphate, sulfate, methane, and TOC. A peristaltic pump with a timer was connected to each IC to control the pumping rates and volumes. The IC columns were pumped and monitored for 15 days between April 16 and May 1, 2008. During this time, the pump times and pump volumes were recorded and the field parameters were measured. Due to a storm and the resulting loss of electricity, the pumps did not operate for approximately three days during the test period. During the test, except during power loss, the pumps were operated at a flow rate of approximately 10 mL/min, cycled on every 3 or 4 hours for 2 to 3 minutes.

Both columns were driven to a depth of 6.5 feet below the creek bottom. Assuming slight compaction of the soil occurred inside the columns during driving, the pore volume of the columns was calculated to be approximately 7 liters assuming the effective porosity of the soil in the column was 20 percent. The pump cycles were sometimes modified to stabilize the flow rate. The test design included pumping until one complete pore volume (PV) of approximately 7,100 mL had been removed from each IC. During the pumping period, approximately 5,110 mL of water were removed from IC-1 and 1,078 mL of water were removed from IC-3. The laboratory results from the *in situ* biodegradation study are summarized in **Table 6-11**.

	Table 6-11									
Analy	Analytical Results of Groundwater Samples Collected from In Situ Columns during Pumping									oing
Well ID			Perchlorate		Chloride	Bromide	Nitrate	Nitrite	Sulfate	TOC
	Sample	Sample	Method 314	Method 332						
	Date	Time	(µg/L)	(µg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Column 3										
(IC-3)	8/8/07	NA	< 1	0.06	290	0.9	< 0.5	< 0.5	55	6.2
	12/18/07	NA	< 1	NA	450	1.4	< 0.5	< 0.5	81	NA
	4/15/08	1:00 PM	<1	NA	220	0.8	< 0.5	< 0.5	39	6.8
	4/18/08	8:35 AM	1,300	NA	NA	NA	NA	NA	NA	NA
	4/23/08	2:20 PM	<1	NA	NA	NA	NA	NA	NA	NA
	4/28/08	8:00 AM	570	NA	NA	NA	NA	NA	NA	NA
Column 1										
(IC-1)	8/9/07	NA	< 1	NA	360	1.0	< 0.5	< 0.5	54	6.6
	12/18/07	NA	< 1	NA	560	1.9	2.3	< 0.5	110	NA
	4/15/08	12:50 PM	<4	NA	33	< 0.5	1.1	< 0.5	18	4.7
	4/16/08	7:40 AM	<1	NA	NA	NA	NA	NA	NA	NA
	4/18/08	8:30 AM	<1	NA	NA	NA	NA	NA	NA	NA
	4/23/08	2:30 PM	750	NA	NA	NA	NA	NA	NA	NA
	4/28/08	8:00 AM	<1	NA	NA	NA	NA	NA	NA	NA
	5/1/08	8:00 AM	40	NA	NA	NA	NA	NA	NA	NA

NA = Not Analyzed

During the test, samples were collected from the sampling port or outlet and analyzed for perchlorate and parameters as described above. The perchlorate concentrations entering the bottom of the column (inlet) were assumed to be equal to measured concentrations in TP-7 (3,200 μ g/L) and TP-3 (2,700 μ g/L) which were the immediately adjacent to the ICs and screened at the same vertical interval. However, because only 15% of the PV in IC-3 had actually been pumped, IC-3 was not used for calculations of biodegradation rates. Since 72 % of the PV in IC-1 was pumped, further evaluation of the biodegradation rates in the Littoral Zone was performed on data from this IC.

The biodegradation rates in IC-1 were estimated by comparing the change in the perchlorate concentration at the column inlet (i.e., 3,200 μ g/L) and with the perchlorate concentration measured at the *in situ* column sampling point or outlet taking into the amount of pumping time. To account for possible dilution within the column, a "worst case" dilution by volume was calculated based on the concept that any water pumped out the column was replaced with surface water. Although there was no evidence to suggest that IC-1 was leaking during the test, to be conservative in the analysis, the worst case scenario was used in the calculation of the biodegradation rate. It was assumed that if 40% of the volume of the column was removed by pumping, and 40% of the column was replaced with surface water, then the starting concentration within the column would be ~60% of the inlet groundwater concentration of 3,200 μ g/L, which would be 1,920 μ g/L.

First-order biodegradation rates (k) were estimated from the following first-order equation (Newell et al., 2002):

$$[C] = [C_o]e^{-kt}$$

Where: [C] = concentration measured at the top of the IC $[C_o]$ = presumed concentration at the bottom of the column corrected for "worst-case" dilution by surface water. "t" = pump time

Corresponding perchlorate first-order half-lives were calculated from:

$$t_{1/2} = 0.693/k$$

For comparison, zero-order degradation rates were calculated using the following equation:

$$[C] = [C_o] - Kt$$

The results for IC-1 are summarized in **Table 6-12**. On 4/28/08, the measured concentration [C] was below detection (<1 μ g/L) and rates were calculated using 1 μ g/L to represent this non-detect. First-order rates varied from 0.12 to 0.63/day. In contrast, the zero-order rates were more consistent, varying from 90 to 150 μ g/L/day.

	Table 6-12							
	Biodegradation Rates Calculated from In Situ Biodegradation Study at IC-1							
	t			[C]	$[C_0]$	k	t 1/2	k
Date Sampled	Total Pump Time (hrs)	Total Volume Pumped ⁽²⁾ (ml)	% Dilution by Volume	Measured Perchlorate Concentration (μg/L)	Calculated Starting Concentration (µg/L) ⁽³⁾	1 st -Order Rate (per day)	1 st - Order Half- Life (days)	Zero- Order Rate (µg/L/d)
4/23/2008	190	2,863	40	754	1,920	0.12	5.8	150
4/28/2008	274	4,093	58	<1	1,344	0.63	1.1	120
5/1/2008	338	5,110	60	40	1,280	0.25	2.8	90

- (1) Assumes that volume of water pumped is replaced with surface water causing dilution.
- (2) Total column volume is 7,100 mL
- (3) If starting concentration is 3,200 μ g/L, then diluted concentration is 60% x 3,200 = 1,920 μ g/L (with no biodegradation).

The ambient perchlorate degradation rate is the Littoral Zone was calculated using measured perchlorate concentrations in TP-4, TP-6 and TP-7 (March 30, 2007, Piezometer Group 2) with an estimated vertical flow velocity of 0.06 ft/d. **Table 6-13** shows estimated travel times for groundwater to move upward from ~6.5 ft bgs in TP-7 to ~5 ft bgs in TP-6 (25 days) and upward from ~6.5 ft bgs to ~3 ft bgs in TP-4 (58 days).

Table 6-13						
Summary of Perchlorate Concentrations at Equivalent Time						
Piezometer ID	Perchlorate (µg/L) ^a	Piezometer Depth (ft bgs)	Equivalent Travel Time (days) ^b			
TP-7	3,200	6.5	0			
TP-6	3.4	5.0	25			
TP-4	6.7	3.0	58			

- a. Perchlorate concentrations reported on March 30, 2007.
- b. Calculated as: (Depth of TP-7 minus Depth of target TP)/ vertical flow velocity = # days

The perchlorate concentrations in the piezometers were plotted against the equivalent time to derive a rate of biodegradation that could be compared with the rates estimated from the IC study. As shown in **Table 6-12** and **Figure 6-17**, there is a large decrease in perchlorate concentration between TP-7 (3,200 μ g/L) and TP-6 (3.4 μ g/L) and little change between TP-6 and TP-4 (6.7 μ g/L). The apparent first-order biodegradation rate estimated from the change in perchlorate over the equivalent 25 days travel time from TP-7 to TP-6 was 0.27/d. This field rate is well within the range observed in the *in situ* column study (0.12 to 0.63/d) and similar to the rate observed in the laboratory macrocosms (0.12/d).

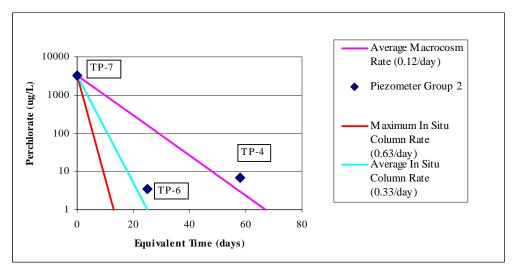


Figure 6-17. Comparison of Macrocosm and In Situ Column Rates

Table 6-14 summarizes the first-order biodegradation rates obtained in the Tier 3 evaluation. The similarity in the observed rates supports the use of macrocosms and *in situ* columns as methods for estimating biodegradation in the natural environment. The results support the information obtained in Tier 1 and 2 as definitive lines of evidence for the natural attenuation of perchlorate.

Table 6-14 Summary of First-Order Biodegradation Rates					
Test	Rate Constant (per day)	Half-Life (days)			
Macrocosms	0.12	5.8			
In Situ Columns	0.12 to 0.63	5.8 to 1.1			
Piezometers	0.27	2.6			

7.0 Performance Assessment

Primary and secondary performance objectives were established in the Technical Demonstration Plan (Solutions-IES, 2006). The ability of MNA to meet these objectives at the Indian Head site is discussed below.

7.1 Primary Performance Objectives.

Criterion: Reduce perchlorate concentration

The perchlorate plume was delineated from the presumed source to Mattawoman Creek. The perchlorate concentration was reduced by >99.9 % during downgradient transport from the source area to Mattawoman Creek. Average concentrations of perchlorate in shallow wells adjoining Mattawoman Creek (TP-1, TP-2, TP-4, and TP-6) were statistically different from wells in the source area (MW-1 and MW-3) at the 95% level.

Criterion: Reduce contaminant mass flux

The results showed natural attenuation rates could be calculated from the source near the hog-out Building 1419 moving southward toward Mattawoman Creek. Mass flux of perchlorate was reduced by > 75% between the most downgradient line of wells in the Land Zone and the Littoral Zone.

Criterion: Factors Affecting Performance

The biogeochemical evaluation showed that conditions in the land wells can be expected to result in limited perchlorate biodegradation. In contrast, biogeochemical conditions in the shallow Littoral Zone wells are excellent for perchlorate biodegradation.

Criterion: Ease of Use

The monitor well network was expanded from six to 39 additional monitoring wells/piezometers. The wells on the land were adequate to collect representative groundwater samples; new wells and piezometers installed on the land and into the creek sediments provided additional monitoring points from which to monitor changes in four geomorphological zones and collect samples from different depths in each zone.

Wells/piezometers were relatively simple to install, although some additional effort and health & safety-related precautions were required to install them in the creek bottom. Wells were not replaced during the demonstration, but placing wells in the creek would eventually become problematic.

Criterion: Maintenance

No special operation and/or maintenance steps were needed to maintain the network for the duration of the study.

7.2 Secondary Performance Objectives

Criterion: Biodegrade Perchlorate

There are a variety of conventional and innovative methods available to demonstrate perchlorate biodegradation including biogeochemical monitoring, MBTs, microcosm and macrocosm studies, *in situ* column experiments, and monitoring for compound specific stable isotopes. Except for

stable isotopes, these techniques were used extensively and effectively in the Indian Head demonstration to confirm bioactivity as a line of evidence for MNA. Biogeochemical parameters indicated good conditions for perchlorate biodegradation in the Littoral zone. This was supported by qPCR measurements showing very high numbers of perchlorate degraders in this same zone. Perchlorate degradation rates were measured in the macrocosms and *in situ* columns were consistent with field observations.

Criterion: Meet Regulatory Standards

Perchlorate concentrations were reduced from over $10,000 \,\mu\text{g/L}$ in the source area to below the USEPA preliminary remediation goal of $24.5 \,\mu\text{g/L}$ prior to discharge to Mattawoman Creek. Concentrations were also frequently, but not always, reduced to below the Maryland Department of Environment (MDE) drinking water standard of $2.6 \,\mu\text{g/L}$.

Criterion: Contaminant Mobility

Implementation of the MNA evaluation did not have any detectable impact on contaminant mobility. Significant amounts of water were not withdrawn or injected into the aquifer, so assessment activities did not impact contaminant mobility.

Site hydrology and associated transport processes did have a major impact on how the MNA evaluation was conducted. Diurnal tidal fluctuations influence the rate of perchlorate discharge to Mattawoman Creek. Extensive studies were conducted to document these effects and to account for the potential for dilution of perchlorate by mixing contaminated groundwater with surface water.

Criterion: Process Waste and Hazardous Materials

MNA is a passive remedial strategy. Therefore waste generation was limited to soil cuttings from well installation and groundwater from well development and purging. Perchlorate assessment and remediation activities can be conducted without extraordinary health and safety handling precautions. MNA does not produce or use hazardous materials as part of the treatment technology. Level D PPE provides adequate protection.

Criterion: Reliability, Versatility and Scale-up Constraints

When site conditions are appropriate, MNA provides a reliable and versatile approach for management of perchlorate plumes. The successful demonstration of MNA requires a monitoring well network designed to illustrate attenuation downstream from the source and prior to intercepting sensitive receptors. There are no scale-up restraints since the MNA evaluation is conducted at full scale.

8.0 Cost Assessment

8.1 Cost Drivers

Costs associated with various *in situ* remediation technologies for perchlorate are discussed in Stroo and Norris (2009) and Krug et al. (2009), but neither directly addresses or compares potential costs to MNA. There are many similarities, particularly associated with up-front assessment and long-term monitoring activities, but the difference with MNA is the absence of any designed intervention with the groundwater conditions. To employ MNA, the goals of the assessment should merge with the goals of MNA. When considering MNA as a remedial alternative, an expanded network of monitoring wells may be installed during the assessment phase to characterize the contaminant distribution and site hydrogeology. Once installed, altering the site monitoring program may be needed to gather additional data to complete the Tier 1 and Tier 2 evaluations. Tier 3 biodegradation rate studies may be helpful for demonstrating perchlorate biodegradation at unusual sites, but may not be necessary in many cases.

The Remedial Action Objectives (RAO) for a site also can have a significant impact on cost and potential applicability of MNA as a remedial alternative. End users should work closely with regulators during the evaluation process to determine realistic objectives for perchlorate remediation that are agreeable to the stakeholders. Results should be achievable for the regulatory agency involved in the cleanup. Cost estimates in the following sections use the federal TBC of 24.5 μ g/L as the target RAO. Natural attenuation rates estimated for the upland portions of the aquifer at the Indian Head site used 24.5 μ g/L as the target RAO (Section 6.1.2). More and more agencies are promulgating standards for perchlorate to take the place of the TBC concentration. For example, during the course of this demonstration the MDE established a perchlorate drinking water standard of 2.6 μ g/L (MDE, 2008).

8.2 Indian Head Demonstration Costs and Long-term Cost Model

When estimating the cost of implementing MNA for the base case, we assumed that a tiered evaluation including all three tiers is required. However, at many sites, a Tier 3 evaluation may not be required. After the tiered evaluation, and assuming the monitoring well network is in place, the primary cost driver for MNA of perchlorate is long-term monitoring.

Table 8-1 summarizes the life-cycle cost components of the Indian Head site. The layout of the table is derived from Krug et al. (2009). The table includes both known costs associated with implementing the demonstration and estimated costs for going forward with MNA at this site. The level of assessment associated with the demonstration completed at the Indian Head site was likely beyond that which might be required for a typical site. However, to accurately portray the overall costs, the actual costs associated with monitoring wells that were installed in the Land Aquifer and in the Littoral Zone and Subtidal Channel are included. The costs associated with the tiered evaluation are also included.

The costs for preparing the present report overlap with an estimate of the costs that would be incurred to take the data derived from this demonstration and use them to prepare a permit application for MNA for the site and gain regulatory approval of this technology as the long-term groundwater remedy. Long-term costs include semi-annual monitoring and reporting. The Net Present Value of the estimated costs is calculated for up to 30 years using a 2.7% interest rate.

Table 8-1 Actual and Estimated Future Costs for Implementation of Perchlorate MNA for the Indian Head Site

	2005	2006	2007	2008	2009	2010						
				Yearly Co	sts Incurred	1						
	1	2	3	4	5	6	7	8	9	10 to 30	NPV of Cost	Total Costs
CAPITAL COSTS												
Complete Assessment on Land	41,400											
Subtidal Channel Assessment		14,700										
Littoral Zone Assessment			20,900									
SUBCOST (\$)	41,400	14,700	20,900	0	0	0	0	0				
TIERED EVALUATION												
Tier 1			11,000									
Tier 2				3,900								
Tier 3					5,200							
Evaluation												
Reporting/Permitting					24,000							
SUBCOST (\$)	41,200	14,700	31,900	3,900	29,200						112,700	120,900
PERFORMANCE MONITORING COSTS (1)												
Sampling/Analysis/Reporting		27,200	27,600	27,100		54,600 ⁽²⁾	54,600	54,600	54,600	54,600 every year		
SUBCOST (\$)		27,200	27,600	27,100		54,600	54,600	54,600	54,600	1,147,500	986,200	1,447800
TOTAL COST (\$)	41,200	41,900	59,500	31,000	29,200	54,600	54,600	54,600	54,600	1,147,500	1,098,900	1,568,700
N												

Notes:

(1) Project Semi-annual monitoring starting in 2010

(2) Average monitoring cost

NPV-Net Present Value; calculated based on 2.7% discount rate

8.3 Cost Comparison: MNA vs. Passive In Situ and Active Pumping Technologies

8.3.1 Basis of Cost Comparison

To compare costs directly between the several remediation scenarios, a base case was prepared using hypothetical site conditions. The characteristics summarized in **Table 8-2** are those used by Krug et al. (2009) and were used for this evaluation in order to simplify the comparison with MNA.

Table 8-2 Summary of Site Characteristics and Design Parameters for Biological Treatment of Perchlorate-Impacted Groundwater

(Source: Krug et al., 2009)

Design Parameter	Units	Characteristics
Plume Width	feet	400
Plume Length	feet	800
Porosity		0.25
Gradient		0.008
Hydraulic Conductivity	ft/d	2.83
Upgradient Perchlorate Concentrations	μg/L	2,000
Downgradient Perchlorate Concentrations	μg/L	1,100
Nitrate Concentration	mg/L	15
Dissolved Oxygen Concentration	mg/L	5
Depth to Water	ft bgs	10
Vertical Saturated Thickness	ft	30
Groundwater Seepage Velocity	ft/year	33
Perchlorate Treatment Objective	μg/L	24.5
Assumed Number of Pore Volumes to Flush Plume		2
Number of Barriers Perpendicular to Groundwater Flow		1
Groundwater Travel Time to Barriers	years	24
Years to Clean Up Groundwater	years	48

The cost estimate for the base case includes an estimate of capital cost, operations and maintenance, and long-term monitoring for the treatment of base case perchlorate plume. Capital costs for the engineered remediation systems include system design, well installation, start-up and testing. Pre-remedial investigations including treatability studies were not included in the capital cost for the engineered remediation systems. However, a tiered evaluation (Tier 1, 2 & 3) and reporting were included with the capital costs for the perchlorate MNA estimate because the tiered evaluation may not be included in typical pre-remedial activities.

Tables 8-3 through 8-5 summarize the life cycle cost for the Passive Injection Biobarrier, the Extraction and Treatment System, and Perchlorate MNA alternatives, respectively, as applied to the Base Case site conditions.

Table 8-3
Cost Components for Passive Injection Biobarrier Treatment of Perchlorate-Impacted Groundwater (Source: Krug et al., 2009)

			y		NPV* of	Total Costs				
	1	2	3	4	5	6	7	8 to 30	Cost	
CAPITAL COSTS										
System Design	68,100								68,100	68,100
Well Installation (30 1" PVC Wells)	32,713								32,713	32,713
Substrate Injection	175,784								175,784	175,784
Start-up and Testing**									0	0
SUBCOST (\$)	276,597	0	0	0	0	0	0	0	276,597	276,597
OPERATION AND MAINTENANCE										
COSTS										
Substrate Injection				166,284			166,284	166,284	985,956	1,496,556
								every		
								3 yrs		
SUBCOST (\$)	0	0	0	166,284	0	0	166,284	166,284	985,956	1,496,556
LONG TERM MONITORING COSTS										
Sampling/Analysis/Reporting	35,240	35,240	35,240	35,240	35,240	11,780	11,780	11,780	348,483	470,700
(Quarterly through 5 years then Annually)								every yr		
SUBCOST (\$)	35,240	35,240	35,240	35,240	35,240	11,780	11,780	11,780	348,483	470,700

TOTAL COST (\$)	311,837 35,240	35,240 201,524	35,240 11,780	178,064	178,064	1,611,036	2,243,853

^{*}NPV- Net Present Value calculated based on 3% discount rate.

^{**&}quot;No Start-up and Testing" costs are included because no operating equipment is left behind following substrate injection

Table 8-4 Cost Components for Extraction and Treatment of Perchlorate-Impacted Groundwater (Source: Krug et al., 2009)

			Voon	Cost is Inc	umnad			NIDV of	Total Costs
	1	2	3	4	5	6	7 to 30	NPV of Cost	Costs
CADITAL COCTO	1	4	3	4	3	6	7 10 30	Cost	
CAPITAL COSTS	00.514							00 -11	00 -11
System Design	90,611							90,611	90,611
Well Installation	86,292							86,292	86,292
System Installation	292,362							292,362	292,362
Start-up and Testing	25,000							25,000	25,000
SUBCOST (\$)	494,265	0	0	0	0	0	0	494,265	494,265
OPERATION AND MAINTENANCE									
COSTS									
System Operation and Maintenance	49,009	74,009	74,009	74,009	74,009	74,009	74,009	1,469,127	2,195,270
							every		
							year		
SUBCOST (\$)	49,009	74,009	74,009	74,009	74,009	74,009	74,009	1,469,127	2,195,270
LONG TERM MONITORING COSTS									
Sampling/Analysis/Reporting	35,240	35,240	35,240	35,240	35,240	11,780	11,780	348,483	470,700
		•	•	•	•	·	every	•	
(Quarterly through 5 years then Annually)							year		
SUBCOST (\$)	35,240	35,240	35,240	35,240	35,240	11,780	11,780	348,483	470,700

TOTAL COST (\$)	578,514	109,249	109,249	109,249	109,249	85,789	85,789	2,311,875	3,160,235

^{*}NPV-Net Present Value calculated based on a 3% discount rate.

Table 8-5 Cost Components for Perchlorate MNA

				Year Cost				NPV of Cost	Total Costs			
	1	2	3	4	5	6	7	8	9	10 to 30	Cost	
CAPITAL COSTS												
System Design	10,000											10,000
Install Expanded Well Network	15,000											15,000
Tier 1, 2, 3 Evaluation	20,000											20,000
Installation/Start-up Testing	0											0
MNA Permit & Reporting	24,000											24,000
SUBCOST (\$)	69,000										67,185	69,000
LONG TERM MONITORING COSTS												
(Quarterly for 5 years then, annually)	46,000	\$94,800	\$94,800	\$94,800	\$94,800	\$23,000	\$23,000	\$23,000	\$23,000	\$23,000 every yr		\$1,000,200
SUBCOST (\$)	\$46,000	\$94,800	\$94,800	\$94,800	\$94,800	\$23,000	\$23,000	\$23,000	\$23,000		752,947	\$1,000,200

_												
	TOTAL COST (\$)	\$115,000	\$94,800	\$94,800	\$94,800	\$94,800	\$23,000	\$23,000	\$23,000	\$23,000	820,320	\$1,069,200

^{** &}quot;No Start-up and Testing" costs are included because no operating equipment is left behind following substrate injection

Table 8-6
Summary of Capital Costs and NPV of Costs for Operation, Maintenance and Monitoring for Biological Treatment of Perchlorate-Impacted Groundwater

Alternative	Capital Costs	NPV of 30 Years of O&M Costs	NPV of 30 Years of Monitoring Costs	NPV of 30 Years of Total Remedy Costs	Total 30- Year Remedy Costs
		Included with			
Perchlorate MNA	\$69	monitoring	\$753	\$820	\$1,069
Passive Injection					
Biobarrier	\$280	\$990	\$350	\$1,610	\$2,240
Extraction and					
Treatment	\$490	\$1,470	\$350	\$2,310	\$3,160

Note: Costs in thousands of dollars.

Table 8-6 summarizes the estimated costs for the three technologies described in **Tables 8-3, 8-4** and **8-5**. Perchlorate MNA is approximately one half the life-cycle cost of the Passive Injection Biobarrier alternative, and approximately one third the cost the Extraction and Treatment alternative even though the cost of monitoring is almost double the long-term monitoring for the engineered systems. The expectation would be similar at the Indian Head site.

9.0 Implementation Issues

9.1 Environmental Checklist

The environmental checklist includes a number of items that are useful both before and during the evaluation of a perchlorate-contaminated site for MNA. In general, the before proceeding down the path toward, it is important to plan an approach to obtain the following key information:

- ➤ Identification of the source area
- > Time of release
- ➤ Historical Data
- ➤ Plume Delineation
- > Sensitive Receptors
- > Subsurface Geochemistry
- ➤ Subsurface Microbiology

Once a plan has been developed, data gaps can be addressed in order to complete the steps outlined in the tiered evaluation of MNA.

9.2 Other Regulatory Issues

The groundwater criteria for many CoCs is well documented, but the recent information gathered about perchlorate at a wide range of sites nationwide has lead to new interest in the issues associated with human health, and its environmental fate and transport. However, regulatory standards for perchlorate in groundwater have not been established in all states. For example at the beginning of this project, Maryland did not have a drinking water or groundwater standard for perchlorate. The federal TBC remains $24.5 \mu g/L$. Maryland issued a drinking water advisory limit $1.0 \mu g/L$ which was recently replaced with a standard of $2.6 \mu g/L$ (MDE, 2008). Other states are in the process of developing standards.

9.3 End-User Issues

Potential end users of the technology include a variety of agencies within the federal government (Dept. of Defense, Dept. of Energy, and Environmental Protection Agency), state and local governments, and private industry. Potential end user concerns may include:

- Permitting
- > Community acceptance
- > Receptors
- > Confirm state specific target concentrations when considering MNA.
- > Potentially long life cycles

Local concerns about perchlorate, the threat of perchlorate and the acceptance of MNA of perchlorate may vary. We have demonstrated that under the proper conditions and with a strategically planned, step-wise approach, end-users can gain assurance that MNA of perchlorate will be protective of human health and the environment.

10.0 References

- Bender, K.S., S.M. O'Connor, R. Chakraborty, J.D. Coates, and L.A. Achenbach, 2002. Sequencing and Transcriptional Analysis of the Chlorite Dismutase Gene of *Dechloromonas agitata* and Its Use as a Metabolic Probe. *Appl. Environ. Microbiol.* 68(10): 4820-4826.
- Borden, R.C., M.J. Hunt, M.B. Shafer and M.A. Barlaz, 1997. *Environmental Research Brief-Anaerobic Biodegradation of BTEX in Aquifer Material*. EPA/600/S-97/003, US Environ. Protect. Agency, Washington, DC, pp. 9.
- Bokuniewicz, H. J., 1992. Analytical Descriptions of Subaqueous Groundwater Seepage. *Estuaries* 15(4): 458-464.
- CDHS (California Department of Health Services), 2007. Maximum Contaminant Levels Inorganic Chemicals. 22 California Code of Regulations §64431.
- Chaudhuri, S.K., S.M. O'Connor, R.L. Gustavson, L.A. Achenbach, and J.D. Coates, 2002. Environmental Factors that Control Microbial Perchlorate Reduction. *Appl. Environ. Microbiol.* 68(9): 4425-4430.
- Coates, J.D. and L.A. Achenbach, 2004. Microbial Perchlorate Reduction: Rocket Fuelled Metabolism. *Nat. Rev. Microbiol.* 2: 569-580.
- Coates, J.D. and L.A. Achenbach, 2006. *Chapter 12: The Microbiology of Perchlorate Reduction and its Bioremediative Application*. In: B. Gu and J.D. Coates (eds.)

 <u>Perchlorate: Environmental Occurrence, Interactions, and Treatment</u>, Springer. <u>pp. 279-295</u>. ISBN: 978-0-387-31114-2.
- Coates, J.D and W.A. Jackson, 2009. Chapter 3, Principles of Perchlorate Treatment. *In* Stroo, H.F and Ward, C.H. (eds). *In Situ* Bioremediation of Perchlorate in Groundwater. Doi:10.1007/978-0-387-84921-8_1, Springer Science + Business Media, LLC, pp. 29-52.
- Coates, J.D., U. Michaelidou, R.A. Bruce, S.M. O'Connor, J.N. Crespi, and L.A. Achenbach, 1999. Ubiquity and Diversity of Dissimilatory (Per)chlorate-Reducing Bacteria. *Appl. Environ. Microbiol.* 65 (12): 5234-5241.
- Coates, J.D. and J. Pollock, 2003. Potential for *In Situ* Bioremediation of Perchlorate in Contaminated Environments. Presented at: *In Situ* and On-Site Bioremediation, the Seventh International Symposium, Orlando, FL, June 2003.
- Cramer, R.J, C. Yates, P Hatzinger and J. Diebold, 2004. Field Demonstration of *In Situ* Perchlorate Bioremediation at Building 1419. NOSSA-TR-2004-001, January 22, 2004.

- ESTCP, 2006. Field Demonstration and Validation of a New Device for Measuring Groundwater and Perchlorate Fluxes at IHDIV-NSWC, Indian Head, MD. Prepared by Purdue University and University of Florida, Project No. ER-0114, Environmental Security Technology Certification Program, Arlington, VA, July 2006.
- ESTCP, 2007. Field and Laboratory Evaluation of the Potential for Monitored Natural Attenuation of Perchlorate in Groundwater, Final Technical Report. Prepared by Solutions-IES, Inc. and North Carolina State University, Project No. ER-0428, Environmental Security Technology Certification Program, Arlington, VA, July 2007.
- ESTCP, 2008. Natural Attenuation of Perchlorate in Groundwater: Processes, Tools and Monitoring Techniques. Prepared by Solutions-IES, Inc., Project No. ER-0428, Environmental Security Technology Certification Program, Arlington, VA, August 2008.
- Farhat, S.K., C.J. Newell and E.M. Nichols, 2006. User's Guide: Mass Flux Tool Kit. Available at http://www.estcp.org/Technology/upload/ER-0430-MassFluxToolkit.pdf
- Gunawan, C., 2007. *Bioremediation for Perchlorate-contaiminated Groundwater*. Michigan State Univ., Microbiology & Molecular Genetics, Course 445. Basic Biotechnology eJournal 3: 6-13. http://www.taxonomicoutline.org/index.php/mmg445/article/view/220/274.
- Hatzinger, P.B., 2005. Perchlorate Biodegradation for Water Treatment. *Environ. Sci Technol.* 39: 239A-247A.
- Herman, D.C. and W.T. Frankenberger, Jr., 1998. Microbial-Mediated Reduction of Perchlorate in Groundwater. *J. Environ. Qual.* 27: 750-754.
- Hiortdahl, S.N., 1997. Geologic Framework, Hydrogeology and Ground-Water Quality of the Potomac Group Aquifer System, Northwestern Charles County, Maryland, USGS Water-Resources Investigations Report 91-4059. Baltimore, Maryland.
- Hoponick, J.R., 2006. Status Report on Innovative *In Situ* Remediation Technologies Available to Treat Perchlorate-Contaminated Groundwater. USEPA, Office of Superfund Remediation & Technology Innovation, Technology Innovation & Field Services Division, Washington, DC, August 2006.
- ITRC (Interstate Technology & Regulatory Council), 2002. A Systematic Approach to *In Situ* Bioremediation in Groundwater Including Decision Trees on *In Situ* Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate. *In Situ* Bioremediation Team. Washington, D.C., Interstate Technology & Regulatory Council, August 2002.
- ITRC (Interstate Technology & Regulatory Council), 2005. Perchlorate: Overview of Issues, Status, and Remedial Options. PERCHLORATE-1. Washington, D.C., Interstate Technology & Regulatory Council, Perchlorate Team, September 2005. (http://www.itrcweb.org).

- Krauter, P.W., B. Daily, V. Dibley, H. Pinkart and T. Legler, 2005. Perchlorate and Nitrate Remediation Efficiency and Microbial Diversity in a Containerized Wetland Bioreactor. *Internat. J. Phytoremed.* 7:113-128
- Krug, T.A., C Wolfe, R.D. Norris and C.J. Winstead, 2009. Chapter 10, Cost Analysis of *In Situ* Perchlorate Remediation Technologies. *In:* Stroo, H.F. and Ward, C.H. (eds.), *In Situ* Bioremediation of Perchlorate in Groundwater. SERDP and ESTCP Remediation Technology Monograph Series, Springer Science+Business Media, LLC, New York, NY, pp 199-218.
- Li, H., M.C. Boufadel, and J.K. Weaver, 2008. Tide-Induced Seawater-Groundwater Circulation in Shallow Beach Aquifers. *J. Hydrol.* 352: 211-224.
- Li, H. and J.J. Jiao, 2003. Review of Analytical Studies of Tidal Groundwater Flow in Coastal Aquifer Systems. *In:* Proceedings of the International Symposium on Water Resources and the Urban Environment. Wuhan, P.R. China, Nov 9-10, p 86-91.
- Logan, B.E, 2001. Assessing the Outlook for Perchlorate Remediation. *Environ. Sci. Technol.* 35 (23): 482A- 487A.
- Logan, B.E., J. Wu and R.F. Unz, 2001. Biological Perchlorate Reduction in High-Salinity Solutions. *Wat. Res.* 35 (12): 3034-3038.
- Lorah, M.M. and L.D. Olsen, 1999. Natural Attenuation of Chlorinated Volatile Organic Compounds in a Freshwater Tidal Wetland: Field Evidence of Anaerobic Biodegradation. *Water Resources Res.* 35 (12): 3811-3827.
- Lorah, M.M., L.D. Olsen, B.L. Smith, M.A. Johnson, and W.B. Fleck, 1997. Natural Attenuation of Chlorinated Volatile Organic Compounds in a Freshwater Tidal Wetland, Aberdeen Proving Ground, Maryland. USGS Water-Resources Investigations Report 97-4171. 95p.
- MADEP (Massachusetts Department of Environmental Protection), 2006. Inorganic Chemical Maximum Contaminant Levels, Monitoring Requirements and Analytical Methods. 310 Code Massachusetts Regulations §22.06.
- Magnus XC, 2005. Energetics Degradation. phA Environmental Restoration, Inc. http://phaer.com/magnusXC.html.
- McKelvie, J.R., S.K. Hirschorn, G. Lacrampe-Coulome, J. Lindstrom, J. Braddock, K. Finnerman, D. Trego and B.S. Lollar, 2007. Evaluation of TCE and MTBE *In Situ* Biodegradation: Integrating Stable Isotope, Metabolic Intermediate, and Microbial Lines of Evidence. *Ground Water Monit. Rev.* 27 (4), 63 -73, Fall 2007)
- MDE (Maryland Department of the Environment), 2008. Cleanup Standards for Soil and Groundwater, Type I and II Aquifers, Interim Final Guidance (Update No. 2.1), June 2008.

- Newell, C.J., H.S. Rifai, J.T. Wilson, J.A. Connor, J.A. Aziz and M.P. Suarez, 2002. Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. United States Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH, EPA/540/S-02/500, November 2002.
- Newell, C.J., J.A. Conner and D.L. Rowen, 2003. Groundwater Remediation Strategies Tool. Prepared for American Petroleum Institute, Regulatory Analysis and Scientific Affairs Department, Publication No. 4730, December 2003.
- Nowicki, B.L., E. Requintina, D. Van Kueren and J. Portnoy, 1999. The Role of Sediment Denitrification. I. Reducing Groundwater-Derived Nitrate Inputs to Nauset March Estuary, Cape Cod, Massachusetts. Estuaries 22 (2A): 245-259.
- NRC, 2005. Health Implications of Perchlorate Ingestion. National Academies Press, Washington, DC, USA, 276p.
- Nzengung, V.A., M.T. Lieberman, H.F. Stroo and P.J. Evans, 2008. Chapter 11, Emerging Technologies for Perchlorate Bioremediation. *In:* Stroo, H.F. and C.H. Ward (Eds). *In Situ* Bioremediation of Perchlorate in Groundwater. doi: 10.1007/978-0-387-84921-8_11. Springer Science + Business Media, LLC.
- Portnoy, J.W., B.L. Nowicki, C.T. Roman and D.W. Urish, 1998. The Discharge of Nitrate-Contaminated Groundwater from Developed Shoreline to Marsh-Fringed Estuary. *Water Resources Res.* 34 (11): 3095-3104.
- Rectanus, H.V., M.A. Widdowson, F.H. Chapelle, C.A. Kelly and J.T. Novak, 2007. Investigation of Reductive Dechlorination Supported by Natural Organic Carbon. *Ground Water Monit. & Remed.* 27, no.4, Fall 2007, pp 53-62.
- Rikken, G.B., A.G.M. Kroon and C.G. van Ginkel, 1996. Transformation of (Per)chlorate into Chloride by a Newly Isolated Bacterium: Reduction and Dismutation. *Appl. Microbiol. Biotechnol.* 45: 420-426.
- Robertson, W.D., C.J. Ptacek and S.J. Brown, 2007. Geochemical and Hydrogeological Impacts of a Wood Particle Barrier Treating Nitrate and Perchlorate in Ground Water. *Ground Water Monit. & Remed.* 27 (2): 85-95, Spring 2007.
- Robinson, M., D. Gallagher and W. Reay, 1998. Field Observations of Tidal and Seasonal Variations in Groundwater Discharge to Tidal Estuarine Surface Water. *Ground Water Monit. Rev.* Winter 1998: 83-92.
- Solutions-IES, 2006. Evaluation of Potential for Monitored Natural Attenuation of Perchlorate in Groundwater, Technology Demonstration Plan for Building 1419 Site, Naval Surface warfare Center, Indian Head, MD. Prepared for Environmental Security Technology Certification Program (ESTCP), Arlington, VA., May 2006.

- Stroo, H.F., R.C. Loehr, and C.H. Ward, 2009. Chapter 1, *In Situ* Bioremediation of Perchlorate in Groundwater: An Overview. *In:* Stroo, H.F and Ward, C.H. (eds). *In Situ* Bioremediation of Perchlorate in Groundwater. Doi:10.1007/978-0-387-84921-8_1, Springer Science + Business Media, LLC, pp. 1-13.
- Stroo, H.F. and R.D. Norris, 2009. Chapter 5, Alternatives for *In Situ* Bioremediation of Perchlorate. *In:* Stroo, H.F and Ward, C.H. (eds). *In Situ* Bioremediation of Perchlorate in Groundwater. Doi:10.1007/978-0-387-84921-8_1, Springer Science + Business Media, LLC, pp. 79-90.
- Sturchio, N.C., P.B. Hatzinger, M.D. Arkins, C. Suh and L.J. Heraty, 2003. Chlorine Isotope Fractionation during Microbial Reduction of Perchlorate. *Environ. Sci. Technol.* 37 (17): 3859-3863.
- Tan, K., T.A. Anderson and W.A. Jackson, 2004a. Degradation Kinetics of Perchlorate in Sediments and Soils. *Water, Air and Soil Pollut.* 151: 245 259.
- Tan, K., W.A. Jackson, T.A. Anderson and J.H. Perdue. 2004(b). Fate of Perchlorate-Contaminated Water in Upflow Wetlands. *Water Res.* 38: 4173-4185.
- Tan, K., T.A. Anderson and W.A. Jackson. 2005. Temporal and Spatial Variation of Perchlorate in Streambed Sediments: Results from *In-Situ* Dialysis Samplers. *Environ. Pollut.* 136: 283–291.
- Tetra Tech NUS, Inc., 2000. Remedial Investigation Report for IR Site 57, Former Drum Disposal Area, Building 292, Indian Head Division Naval Surface Warfare Center, Indian Head, Maryland. Prepared for the Engineering Field Activity Chesapeake Naval Facilities Engineering Command. Contract No. N62472-90-D-1298, July 2000
- Tobias, C.R., S.A.Macko, I.C. Anderson, E.A Canuel and J.W. Harvey, 2001. Tracking the Fate of a High Concentration Groundwater Nitrate Plume through a Fringing Marsh: A Combined Groundwater Tracer and *In Situ* Isotope Enrichment Study. *Limnol. Oceanogr.* 46(8): 1977-1989.
- Uchiyama, Y., 1999. Coastal Groundwater Flow and Associated Nutrient Transport into the Sea. Presented at: 2nd UJNR/CEST Panel, Charleston, Maryland, Sponsored by NOAA NOS, October 1999.
- USEPA, 1997. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17, Interim Final, November 1997.
- USEPA, 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. EPA/600/R-98/128. Washington, DC: ORD.

- USEPA, 1999. Final Directive: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17P. http://www.epa.gov/swerust1/directiv/d9200417.htm.
- US EPA, 2005. Perchlorate Treatment Technology Update: Federal Facilities Forum Issue
 Paper. EPA No. 542-R05-015. InfoNational Service Center for Environmental
 Protection, Cincinnati, OH.
 (http://yosemite.epa.gov/ncepihom/nsCatalog.nsf/fe334be39822543485256fbf005fe5ec/8
 4308272e16c68dc852570dd0056d0d5!openDocument)
- US EPA, 2006. <u>Assessment Guidance for Perchlorate</u>. Memorandum from S.P. Bodine, Asst. Administrator, to Regional Administrators. January 26, 2006.
- USFDA (U.S. Food and Drug Administration), 2007. 2004-2005 Exploratory Survey Data on Perchlorate in Food. Posted May 2007. http://www.cfscan.fds.gov/~dms/clo4data.html.
- Westbrook, S.J., J.L. Rayner, G.B. Davis, T.P. Clemnent, P.L. Bjerg and S.J. Fisher, 2005. Interaction Between Shallow Groundwater, Saline Surface Water and Contaminant Discharge at a Seasonally and Tidally Forced Estuarine Boundary. *J. Hydrol.* 302: 255-269.
- Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller and J.E. Hansen, 1995. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater, Volume II. Air Force Center for Environmental Excellence, Brooks Air Force Base, TX. November 1995.
- Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, P.E. Haas, R.N. Miller, J.E. Hansen and F.H. Chapelle, 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater. EPA 600-R-98-128.
- Wilson, J.T. Jong S. Cho, Frank P. Beck, 1997. Field Estimation of Hydraulic Conductivity for Assessments of Natural Attenuation. Volume 2 of the Fourth International *In Situ* and On Site Bioremediation Symposium New Orleans, April 28 May 1, 1997. Battelle Press, Columbus OH. pp 309 314

Appendix A **Monitoring Well/Piezometer Construction Details & Select Boring Logs**

Log of Soil BoringSGP-2D

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

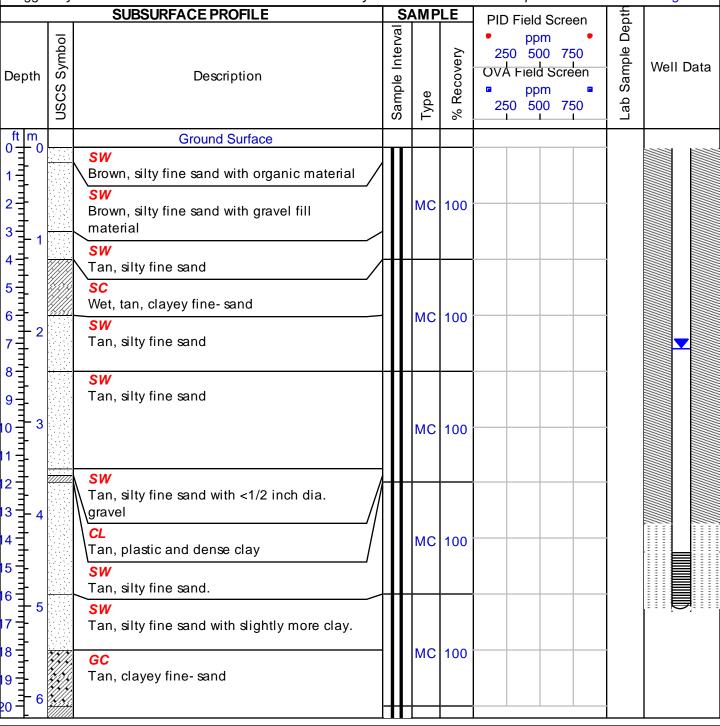
Drilling Method: Geoprobe City: Indian Head

Sampler Type: Macro-Core County: Charles Water Level From TOC: 7.64 feet

Boring Date: 11/15/05 State: Water Level BGS: 7.16 feet

Installed By:

Logged By: DH Checked By: DH Depth of Well: 16.62 feet bgs



Log of Soil BoringSGP-2D

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

Drilling Method: Geoprobe City: Indian Head Initial Water Level: 6 feet Sampler Type: Macro-Core County: Charles Stabalized Water Level: N/A

Boring Date: 11/15/05 Cave In Depth: N/A

Logged By: DH Checked By: DH Total Depth of Boring: 16.62 feet

Logge	d By	: DH Checked By:				Total Depth of Bo	ring:	16.62 feet
		SUBSURFACE PROFILE	S	<u>AMP</u>	LE	PID Field Screen	pth	
Depth	USCS Symbol	Description	Sample Interval	Type	% Recovery	ppm 250 500 750 OVA Field Screen ppm 250 500 750	Lab Sample Depth	Well Data
21 1 22 1 23 1 7 23 1 7 24 1 7		CL Bluish, grey sandy clay		МС	100			
25 =								
		Boring terminated at 24 feet bgs						
8								
₹ / ∃								
28 =								
29 = 9								
30 ₹								
3 1 ₹								
32 =								
33 = 10								
 34								
35 -								
35 - 11								
1 1								
87 - 1								
38 -								
39 = 12								
40 =								

Log of Soil BoringSGP-4D

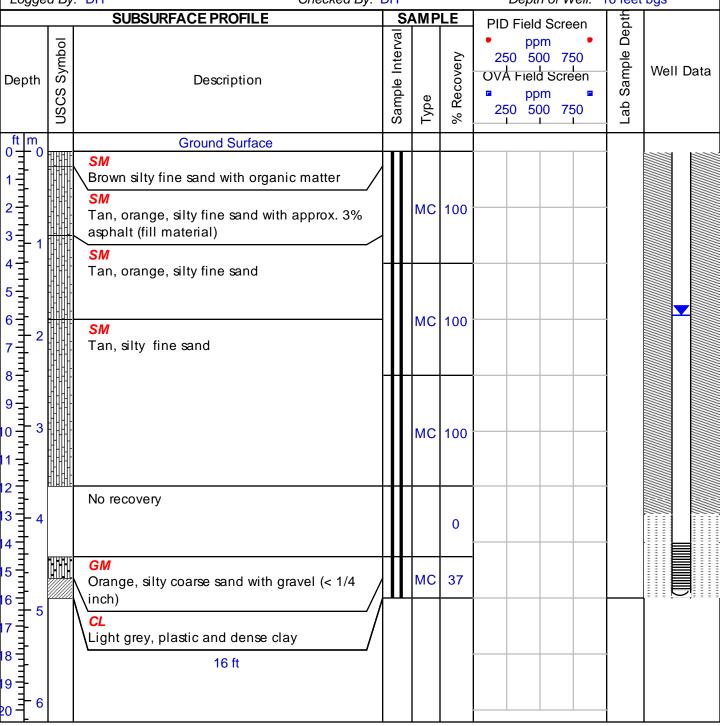
Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

Drilling Method: Geoprobe City: Indian Head

Sampler Type: Macro-Core County: Charles Water Level From TOC: 7.08 feet Boring Date: 11/15/05 State: Maryland Water Level BGS: 5.86 feet

Installed By: Vironex

Logged By: DH Checked By: DH Depth of Well: 16 feet bgs



Log of Soil BoringSGP-6D

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

Drilling Method: Geoprobe City: Indian Head

Sampler Type: Macro-Core County: Charles Water Level From TOC: 7.04 feet

Boring Date: 11/15/05 State: Maryland Water Level BGS: 5.99 feet

Installed By: Vironex

Logged By: DH Checked By: DH Depth of Well: 16 feet bgs

Logge	d By	Checked By:	DH			Depth of Well: 16 feet bgs			
		SUBSURFACE PROFILE	S	AMP	LE	PID Field Screen	pth		
Depth	USCS Symbol	Description	Sample Interval	Type	% Recovery	ppm 250 500 750 OVA Field Screen ppm 250 500 750	Lab Sample Depth	Well Data	
ft m 0 = 0		Ground Surface							
3 1 1		SM Brown, silty fine sand with organic material and gravel SW Red, fine sand with gravel		МС	100				
5 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		SM Tan, orange, silty fine sand (dry) SM Tan, silty fine sand (wet). Low strength zone from 14 to 16 feet. 50% recovery from		МС	100			<u></u>	
8 11 3 12 12 12 12 12 12 12 12 12 12 12 12 12		12 to 16 feet due to 1 inch sized gravel blocking Geoprobe sleeve		МС	100				
13 - 4 14 - 1 15 - 1 16		GM Silty gravel, inferred.		МС	50				
17 17 18 18 19 19 19 19 19 19 19 19 19 19 19 19 19		CL Light tan, plastic and dense clay Boring terminated at 17 feet bgs		МС	100				
20 = 6									

Log of Soil BoringSGP-6D

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

Drilling Method: Geoprobe City: Indian Head Initial Water Level: 7 feet Sampler Type: Macro-Core County: Charles Stabalized Water Level: N/A

Boring Date: 11/15/05 Cave In Depth: N/A

Logged By: DH Checked By: DH Total Depth of Boring: 17 feet

Logge	ed By		Checked By: I				Total Dep	th of Bo	oring:	17 feet
		 SUBSURFACE PROFILE		SA	۱МР	LE	PID Field Scr	een	pth	
Depth	USCS Symbol	Description		Sample Interval	Type	% Recovery	ppm 250 500 7 OVA Field Scr ppm 250 500 7	50 een	Lab Sample Depth	Well Data
21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		21 ft								

Log of Soil BoringSGP-8D Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP Project: Perchlorate MNA Drilling Method: Geoprobe City: Indian Head Sampler Type: Macro-Core County: Charles Water Level From TOC: 19.48 feet Boring Date: 11/15/05 State: Maryland Water Level BGS: 17.21 feet Installed By: Vironex Logged By: DH Checked By: DH Depth of Well: 23 feet bgs SUBSURFACE PROFILE **SAMPLE** Lab Sample Depth PID Field Screen Sample Interval Symbol ppm 250 500 750 Recovery OVA Field Screen Well Data Depth Description USCS 8 ppm 250 500 750 **Ground Surface** SM Brown, silty fine sand with organic material MC 100 Brown, silty fine sand with gravel fill material SM Tan, silty fine sand MC 100 SC Tan, clayey fine sand (wet) Tan, silty fine sand MC 100 Tan, silty fine sand **GM** Tan, silty fine sand with <1/2 inch dia. gravel MC 100 CL Tan, plastic and dense clay SM Tan, silty fine sand MC 100 Tan, silty fine sand with slightly more clay SC Tan, clayey fine sand Bluish grey sandy clay MC 100 24 ft Solutions-IES, Inc. 1101 Nowell Road

Raleigh, NC 27607 (919) 873-1060

Log of Soil BoringSGP-15

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

Drilling Method: Geoprobe City: Indian Head

Sampler Type: Macro-Core County: Charles Water Level From TOC: N/A
Boring Date: 06/07/06 State: Maryland Water Level BGS: N/A

Installed By: Vironex

Logged By: SK Checked By: JM Depth of Well: 9.49 feet bgs

99-	и Бу	: SK Checked By:					Deptn of vveil: 9		et bys
		SUBSURFACE PROFILE		SA	MP	LE	PID Field Screen	pth	
Depth	USCS Symbol	Description	Sample Interval	Sample interval	Туре	% Recovery	ppm 250 500 750 OVA Field Screen ppm 250 500 750	Lab Sample Depth	Well Data
ft m		Ground Surface							
		No recovery			МС	0			
3 - 1					МС	0			
4 5 6		CL Grey, silty clay			МС	100			
7 - 2		No recovery			МС	0			
9 10 3		CL Grey clay with some silt			МС	100			
10 7 7 11 11 11 11 11 11 11 11 11 11 11 11		No recovery			МС	0			
12 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -		12 ft							

Log of Soil BoringSGP-20

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Client: ESTCP

Drilling Method: Geoprobe City: Indian Head

Sampler Type: Macro-Core County: Charles Water Level From TOC: N/A Boring Date: 06/08/06 State: Maryland Water Level BGS: N/A

Installed By: Vironex

Logged By: SK Checked By: JM Depth of Well: 6.22 feet bgs

Logge	d By	: SK Checked By:	JM				Depth of Well: 6	.22 fe	et bgs
		SUBSURFACE PROFILE	,	SA	MP	LE	PID Field Screen	oth	
Depth	USCS Symbol	Description	Sample Interval		Туре	% Recovery	ppm 250 500 750 OVA Field Screen ppm 250 500 750	Lab Sample Depth	Well Data
ft m		Ground Surface		丁					
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		OL Grey to black organic clay with fine sand and silt, odor		ı	МС	100			
3 - 1		SC Grey, fine-grained clayey sand		ľ	МС	100			
5 1 1 1 1 1		SC Green, fine-grained sand with some clay		ſ	МС	100			
6 - 2		No recovery		ľ	МС	0			
9 + 3		SC Green, fine- to medium-grained sand with some clay		ľ	МС	100			
10 - 3		10 ft							

Log of Soil BoringSGP-22D

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Boring Number: SGP-22D

Client: ESTCP Page: 1 of 1

Project Location: Naval Surface Warfare Center City: Indian Head, MD County:

Site or Site Area: Channel Well

Drilling Method: Push Date Started: 09/26/06 Date Finished: 09/26/06

Sample Type: Hand Samples Initial Water Level: Final Water Level:

Logged By: JD Checked By: Total Depth of Boring: 10 Total Depth of Well: 8.5 feet bgs

Logg	jea B	<i>y</i> . J	D Спескеа ву: Тотат Deptr	01 6	OHI	g.	10		l otal Depth of We	<i>∃II.</i>	o.s reet bys
			SUBSURFACE PROFILE			MA	PLE		PID Field Screen		
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interva	Туре	Blows per Foot (N)	Recovery	5 15 25 35 45 FID Field Screen ppm 5 15 25 35 45	Lab Sample	
			Ground Surface								
	1 - 2 -		OL Dark Brown to black clayey SILT, high organic content	1		HS		100			
	3		ML Dark brown clayey SILT, with some fine sand	2		HS		100			
	4 = 5 = 5		CL Brown, sandy CLAY SM Dark brown, fine to medium silty	3	$\ $	HS		100			
	6		SAND CL Brown, silty sandy CLAY		#						
	7		SP Brown medium to fine SAND	4		HS		100			
	9			5		HS		0			
	10 =		10 ft								
	11 =										
	12 =										
	13										
	14 =										
	15									 	



Log of Soil BoringSGP-23D

Project: Perchlorate MNA Solutions-IES Project No.: 3030.04A2.ESTC Boring Number: SGP-23D

Client: ESTCP Page: 1 of 1

Project Location: Naval Surface Warfare Center City: Indian Head, MD County:

Site or Site Area: Channel Well

Drilling Method: Push Date Started: 09/27/06 Date Finished: 09/27/06

Sample Type: Hand Samples Initial Water Level: Final Water Level:

Logged By: JD Checked By: Total Depth of Boring: 10 Total Depth of Well: 8.5 feet bgs

Logg	gea B	y. J	D Спескеа ву: Готаї Depth	01 6	OHH	g.	10		l otal Depth of We	<i>;</i> 11.	0.5 leet bys
			SUBSURFACE PROFILE				PLE		PID Field Screen		
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interva	Туре	Blows per Foot (N)	Recovery	A ppm A 5 15 25 35 45 FID Field Screen ppm ● 5 15 25 35 45 1	Lab Sample	
	_		Ground Surface								
	1-		OL Black clayey SILT, high organic content	1		HS		100			
	2-		SP Black medium to fine SAND		#						
	3-		ML Dark brown, clayey SILT with little fine sand	2		HS		100			
	5		SM Dark brown, fine silty SAND SP Green, glauconitic, medium to fine SAND	3		HS		100			
	7-		SAND	4		HS		100			
	9-			5		HS		0			
	11 - 12 - 13 - 13 - 1		10 ft								
	14 -										



							PPENDIX A					
		T	4:		Monitor Wel Depth			nstruction Deta	ails	Fl		
Well ID	Diameter (in)	Loca Easting	Northing	Top of Casing (ft above Land Surf).	from TOC to Bottom	Screen Length (ft)	Screen Top (bgs)	Screen Bottom (bgs)	Land Surface (ft MSL)	Top of Casing (ft MSL)	Top of Screen (ft MSL)	Bottom of Screen (ft MSL)
ID	(111)	Lasting	Northing	Land Surr).				ETERS ON LA		(It WISL)	(It MSL)	(It MSL)
MW-1	2	1265478.00	334658.98	2.50	17.72	10	5.22	15.22	9.05	11.55	3.83	-6.17
MW-2	2	1265504.81	334546.78	2.55	18.67	10	6.12	16.12	8.13	10.68	2.01	-7.99
MW-3	2	1265601.59	334593.57	2.73	17.55	UN	UN	UN	9.65	12.38	4.38	-5.17
MW-4 MW-5	2 2	1265524.71 1265531.18	334600.28 334591.91	0.84 2.63	17.85 19.48	10 10	7.01 6.85	17.01 16.85	8.65 8.60	9.49 11.23	1.64 1.75	-8.36 -8.25
SGP-1S	1	1265596.49	334405.67	3.46	15.86	5	7.40	12.40	4.70	8.16	-2.70	-7.70
SGP-1D	1	1265597.45	334404.40	1.23	16.87	2	13.64	15.64	4.76	5.99	-8.88	-10.88
SGP-2S	1	1265702.87	334447.42	1.60	14.91	5	8.31	13.31	7.23	8.83	-1.08	-6.08
SGP-2D	1	1265704.69	334449.16	0.57	17.10	2	14.53	16.53	7.34 6.04	7.91	-7.19	-9.19
SGP-3S SGP-3D	1	1265786.14 1265785.30	334522.64 334526.57	3.20 1.90	14.97 17.25	5 2	6.77 13.35	11.77 15.35	5.93	9.24 7.83	-0.73 -7.42	-5.73 -9.42
SGP-4S	1	1265558.48	334470.88	3.57	14.55	5	5.98	10.98	6.27	9.84	0.29	-4.71
SGP-4D	1	1265555.75	334471.61	1.64	17.05	2	13.41	15.41	6.27	7.91	-7.14	-9.14
SGP-5S	1	1265695.72	334581.28	3.85	15.00	5	6.15	11.15	8.78	12.63	2.63	-2.37
SGP-5D SGP-6S	1	1265695.13 1265534.10	334578.79 334558.22	2.81 2.46	17.00 15.98	5	12.19 8.52	14.19 13.52	8.68 8.78	11.49 11.24	-3.51 0.26	-5.51 -4.74
SGP-6S SGP-6D	1	1265534.10	334558.22	1.30	15.98	2	13.79	15.79	8.78	10.00	-5.09	-4.74 -7.09
SGP-7S	1	1265637.41	334609.37	3.69	14.93	5	6.24	11.24	9.96	13.65	3.72	-1.28
SGP-7D	1	1265634.83	334610.02	2.68	17.13	2	12.45	14.45	9.99	12.67	-2.46	-4.46
SGP-8S	1	1265472.57	334600.47	3.43	14.97	5	6.54	11.54	7.85	11.28	1.31	-3.69
SGP-8D TP-5	1	1265474.56 NM	334597.69 NM	2.61 1.00	25.08 11.00	5	17.47 5.00	22.47 10.00	7.90 4.02	10.51 5.02	-9.57 -0.98	-14.57 -5.98
TP-8	1	NM	NM	1.00	11.00	5	5.00	10.00	5.60	6.60	0.60	-4.40
								N THE LITTO				
SGP-9	3/4	1265857.10	334467.39	4.31	12.43	2	6.12	8.12	-0.98	3.33	-7.10	-9.10
SGP-19	3/4	1265701.76	334369.94	3.24	11.98	2	6.74	8.74	-0.47	2.77	-7.21	-9.21
SGP-20	3/4	1265591.09	334313.63	3.98	10.20	2	4.22	6.22	-1.08	2.90	-5.30	-7.30
SGP-21	1	1265480.63	334249.70	4.80	12.56	5	2.76	7.76	-1.09	3.71	-3.85	-8.85
TP-1	1	1265705.7	334357.2	2.45	5.45	1	2.00	3.00	-0.68	1.77	-2.68	-3.68
TP-2	1	1265705.7	334357.2	2.45	7.45	1	4.00	5.00	-0.68	1.77	-4.68	-5.68
TP-3 DP-1	1	1265705.7 1265781.7	334357.2 334428.8	2.45 NM	9.12 NM	2	5.67 8.35	6.67 9.35	-0.68 NM	1.77 1.75	-6.35	-7.35
TP-4	1	1265596.9	334300.2	3.02	6.02	1	2.00	3.00	-0.67	NM	-2.67	-3.67
TP-6	1	1265596.9	334300.2	3.02	8.02	1	4.00	5.00	-0.67	NM	-4.67	-5.67
TP-7	1	1265596.9	334300.2	3.02	9.69	1	5.50	6.50	-0.67	NM	-6.17	-7.17
DP-2 DP-3	1	1265596.9 1265535.6	334300.2 334283.8	3.02 NM	12.02 NM	1	8.00 6.00	9.00 7.00	-0.67 NM	NM 2.74	-8.67	-9.67
ISC-1	1	NM	NM	INIVI	INIVI	1	0.00	7.00	INIVI	2.74		
ISC-2	1	NM	NM									
ISC-3	1	NM	NM									
ISC-4	1	NM	NM									l .
				MONITO	RWELLSAN	D PIEZO	METERS IN	THE SUBTIDA	I. CHANNEI			
SGP-22S	1	1265608.75	334272.75	5.03	7.84	1	1.81	2.81	-1.65	3.38	-3.46	-4.46
SGP-22D	1	1265608.08	334272.58	4.27	8.50	1	3.23	4.23	-1.65	2.62	-4.88 (est)	⁴ -5.88
SGP-22SW		1265609.85	334273.21	4.30	NA	1	1.0	0.00	-1.65	2.65	NA	NA
SGP-23S	1	1265715.67	334333.75	4.30	8.38	1	3.08	4.08	-2.11	2.19	-5.19	-6.19
SGP-23D	1	1265715.13	334333.54	5.36	13.75	1	7.39	8.39	-2.11	3.25	-9.50	-10.50
SGP-23SW SGP-24S	1 1	1265715.26 1265865.89	334333.17 334419.54	4.39 4.70	NM 8.55	1	1.00 2.85	0.00 3.85	-2.11 -1.46	2.28 3.24	-4.31	NM -5.31
SGP-24D	1	1265865.32	334419.34	2.83	11.40	1	7.57	8.57	-1.46	1.37	-9.03	-10.03
SGP-24SW	1	1265866.02	334418.83	3.47	NM	1	1.00	0.00	-1.46	2.01	NM	NM
						D PIEZO		THE SUBTIDAL			_	
SGP-10	2	1265846.42	334370.28	4.43	14.83	2	8.40	10.40	-2.02	2.41	-10.42	-12.42
SGP-11 SGP-12	2 2	1265718.39 1265628.97	334316.09 334215.13	4.80 4.57	14.84 14.82	2	8.04 8.25	10.04 10.25	-2.07 -1.59	2.73	-10.11 -9.84	-12.11 -11.84
SGP-12 SGP-13	2	1265628.97	334215.13	5.62	17.15	2	9.53	10.25	-1.59 -1.97	2.98 3.65	-9.84 -11.50	-11.84 -13.50
SGP-14	2	1265728.37	334142.48	5.42	14.84	2	7.42	9.42	-2.13	3.29	-9.55	-11.55
SGP-15	2	1265799.09	334219.15	5.46	14.95	2	7.49	9.49	-2.03	3.43	-9.52	-11.52
SGP-16	2	1265902.09	334267.02	4.43	14.90	2	8.47	10.47	-2.43	2.00	-10.90	-12.90
SGP-17 SGP-18	2	1265851.57 1265687.35	333901.79 333733.42	5.98 5.09	14.21 14.87	2	6.23 7.78	8.23 9.78	-3.00 -1.89	2.98 3.20	-9.23 -9.67	-11.23 -11.67
30P-18		1203087.33	333133.42	3.09	14.8/	- 2	1.18	7./8	-1.89	5.20	-7.0/	-11.0/

2 | 1265687.35 | 33373.42 | 5.09 | 14.87 | 2 | 7.78 |
Survey Data provided by KCI, Inc.
Elevations are based on the NAVD 88 vertical datum
Piezometer and In situ Column locations and elevations were measured from nearby monitor wells.
Piezometer and In Situ Column coordinates are estimated from locations plotted on the basemap
NM = Not Measured
UN- Unknown

Appendix B

Historical Water Level Measurements

APPENDIX B

Groundwater Elevation Data

				Groundy
Well		Depth to Water	Top of Casing Elevation	Groundwater Elevation
ID	Date	(ft)	(ft msl)	(ft msl)
	LAND	MONITORING		()
	11/15/2005	6.02		5.53
MW-1	9/25/2006	5.80	11.55	5.75
	4/15/2008	5.76		5.79
MW-2	11/15/2005	7.78	10.68	2.90
14144 2	9/25/2006	7.42	10.00	3.26
	11/15/2005	9.97		2.41
MW-3	9/25/2006	9.49	12.38	2.89
	4/15/2008	8.92		3.46
3.637.4	11/15/2005	6.24	0.40	3.25
MW-4	9/25/2006	5.79	9.49	3.70
	4/15/2008 11/15/2005	5.24 8.08		4.25 3.15
CPMW-5	9/28/2006	7.75	11.23	3.48
CI WW-5	4/15/2008	7.04	11.23	4.19
	11/16/2005	7.89		0.27
	9/26/2006	7.91		0.25
SGP-1S	8/9/2007	6.74	8.16	1.42
	4/15/2008	7.00	1	1.16
	11/16/2005	5.38		0.61
	9/26/2006	5.76		0.23
SGP-1D	8/9/2007	8.97	5.99	-2.98
	4/15/2008	4.83		1.16
	11/16/2005	8.49		0.34
	9/26/2006	8.68		0.15
SGP-2S	2/8/2007	8.52	8.83	0.31
	8/9/2007	9.36		-0.53
	4/15/2008	8.01		0.82
	11/16/2005	7.64		0.27
	9/26/2006	7.76		0.15
SGP-2D	2/8/2007	7.64	7.91	0.27
	8/9/2007	8.44		-0.53
	4/15/2008	7.13		0.78
	11/16/2005	8.46	1	0.37
SGP-3S	9/26/2006	8.98	8.83	-0.15
	8/9/2007	9.68 8.37	-	-0.85 0.46
	4/15/2008 11/16/2005	7.55		0.46
	9/25/2006	7.64		0.19
SGP-3D	8/9/2007	8.25	7.83	-0.42
	4/15/2008	6.97		0.86
	11/17/2005	8.67		1.17
SGP-4S	9/26/2006	8.83	9.84	1.01
	4/15/2008	7.70		2.14
	11/17/2005	7.08		0.83
SGP-4D	9/26/2006	7.27	7.91	0.64
	4/15/2008	6.27		1.64
	11/17/2005	11.96		0.67
SGP-5S	9/26/2006	11.75	12.63	0.88
	4/15/2008	10.96		1.67
000 50	11/16/2005	10.98	1,, .,	0.51
SGP-5D	9/26/2006	10.85	11.49	0.64
	4/15/2008	10.17	 	1.32
SCD 65	11/17/2005	8.11	11.24	3.13
SGP-6S	9/25/2006 4/15/2008	7.92 7.18	11.24	3.32 4.06
	4/15/2008 11/17/2005	7.18	+	2.96
SGP-6D	9/25/2006	6.58	10	3.42
551-00	4/15/2008	5.90	10	4.10
	11/16/2005	12.07		1.58
SGP-7S	9/25/2006	11.67	13.65	1.98
	4/15/2008	10.88	1	2.77
	11/16/2005	11.25		1.42
SGP-7D	9/25/2006	10.87	12.67	1.80
	4/15/2008	10.12	1	2.55
	11/17/2005	7.33		3.95
SGP-8S	9/25/2006	7.24	11.28	4.04
	4/15/2008	6.71		4.57
	11/17/2005	19.48	1	-8.97
SGP-8D	9/25/2006	6.09	10.51	4.42
	3/29/2007	6.09	1	4.42
	4/15/2008	6.03	l	4.48

tion Data		Donath to	T	C
Well		Depth to Water	Top of Casing Elevation	Groundwater Elevation
	Date	(ft)	(ft msl)	(ft msl)
ID			FORING WELLS	(It IIISI)
	1		TORING WELLS	0.00
	6/8/2006	2.45	-	0.88
SGP-9	9/25/2006	3.36	2 22	-0.03
SGP-9	3/28/2007	2.54	3.33	0.79
	8/8/2007	3.59	4	-0.26
	4/15/2008	2.65		0.68
	6/8/2006	1.94	-	0.83
	9/25/2006	2.64	l	0.13
SGP-19	3/28/2007	1.80	2.77	0.97
	8/8/2007	3.30	_	-0.53
	4/15/2008	1.84		0.93
	6/8/2006	1.70		1.20
SGP-20	9/25/2006	3.16	2.90	-0.26
301-20	3/28/2007	2.48	2.70	0.42
	4/15/2008	2.77		0.13
	9/27/2006	3.29		0.42
GGD 21	3/28/2007	3.42	7	0.29
SGP-21	8/8/2007	3.46	3.71	0.25
	4/15/2008	3.78	1	-0.07
		L MONITORIN	NG WELLS	
	9/27/2006	3.04	1	0.34
	3/28/2007	3.11	-i i	0.27
SGP-22S	8/8/2007	3.04	3.38	0.34
	4/15/2008	2.80	-	0.54
	9/27/2006	2.83	1	-0.21
	3/28/2007	2.38	1	0.24
SGP-22D			2.62	
	8/8/2007	2.25	-	0.37
a an asawı	4/15/2008	2.05	+	0.57
SGP-22SW	0/27/2004	1.02	1	0.26
SGP-23S*	9/27/2006	1.93	2.19	0.26
	4/15/2008	1.32		0.87
	9/27/2006	3.61	_	-0.36
SGP-23D	8/8/2007	3.05	3.25	0.20
	4/15/2008	3.11		0.14
SGP-23SW				
	9/27/2006	3.00	」	0.24
SGP-24S	8/8/2007	3.51	3.24	-0.27
	4/15/2008	2.49		0.75
	9/27/2006	3.25		-0.01
SGP-24D	8/8/2007	1.98	1.37	1.26
	4/15/2008	0.69		0.68
SGP-24SW		2.46		
	MUDFLA	IS MONITORI	NG WELLS	
CCD 10	6/8/2006	1.34	2.41	1.07
SGP-10	9/25/2006	3.31	2.41	-0.90
	6/8/2006	1.61		0.80
SGP-11	9/25/2006	3.61	2.73	-0.88
	6/8/2006	1.79		0.62
SGP-12	9/25/2006	3.73	2.98	-0.75
	6/8/2006	2.51	1	-0.10
SGP-13	9/25/2006	4.54	3.65	-0.89
		1.97	1	0.44
	6/8/2006		3.29	
SGP-14	6/8/2006 9/25/2006		3.27	_() 44
	9/25/2006	4.28		-0.99 0.22
SGP-14 SGP-15	9/25/2006 6/8/2006	4.28 2.19	3.43	0.22
	9/25/2006 6/8/2006 9/25/2006	4.28 2.19 4.54		0.22 -1.11
	9/25/2006 6/8/2006 9/25/2006 6/8/2006	4.28 2.19 4.54 1.01		0.22 -1.11 1.40
SGP-15	9/25/2006 6/8/2006 9/25/2006 6/8/2006 9/25/2006	4.28 2.19 4.54 1.01 2.97	3.43	0.22 -1.11 1.40 -0.97
SGP-15	9/25/2006 6/8/2006 9/25/2006 6/8/2006 9/25/2006 6/8/2006	4.28 2.19 4.54 1.01 2.97 2.04	3.43	0.22 -1.11 1.40 -0.97 0.37
SGP-15	9/25/2006 6/8/2006 9/25/2006 6/8/2006 9/25/2006 6/8/2006 9/25/2006	4.28 2.19 4.54 1.01 2.97 2.04 4.01	3.43	0.22 -1.11 1.40 -0.97 0.37 -1.03
SGP-15	9/25/2006 6/8/2006 9/25/2006 6/8/2006 9/25/2006 6/8/2006	4.28 2.19 4.54 1.01 2.97 2.04	3.43	0.22 -1.11 1.40 -0.97 0.37

^{*} The pipe on SGP-23S is slanted NS-Well not surveyed Survey data provided by KCI, Inc. Elevations referenced to NADV88 ft msl = feet above mean sea level

Appendix C

Performance Monitoring Data

APPENDIX C - TABLE C1 Summary Pre-Demonstration Analytical Results Samples Collected June 6, 7, 8, 2006

	units																
Relative		Littoral	Littoral	Littoral	Average	Subtidal	Subtidal	Subtidal	Subtidal	Subtidal	Subtidal	Subtidal	Subtidal	Subtidal	Average	Surface	Surface
Location		Zone	Zone	Zone	Average	Shallows	Shallows	Shallows	Shallows	Shallows	Shallows	Shallows	Shallows	Shallows	Average	Water	Water
		SGP-9	SGP-19	SGP-20		SGP-10	SGP-11	SGP-12	SGP-13	SGP-14	SGP-15	SGP-16	SGP-17	SGP-18			
Perchlorate	μg/L	200	4,400/4,300(1)	13,000	5,900	ND	ND/ND ⁽²⁾	ND	ND	ND	ND	ND	ND	ND	ND		
Methane	μg/L	ND	ND	120	40	6300	9.9	1,300	8,400	6,200	4,300	12,000	12,000	13,000	7,100		<u> </u>
TOC-soil	mg/kg	7,500	16,000	5,900	9.800	21,000	48,000	50,000 (0.25 ft)/	21,000	18,000	29,000	24,000	34,000	28,000	30,700		1
100 5011	6/6	(2-4ft)	(0-2ft)	(2-4ft)	,,000	(4-6ft)	(0-2ft)	34,000 (1.5 ft)	(1.5ft)	(4-6 ft)	(4-6ft)	(4-6ft)	(0-2ft)	(4-6ft)	20,700		
TOC-soil	mg/kg	1,800	2,500	2,800	2,400	21,000	13,000	86,000	56,000	20,000	44,000	31,000	15,000	24,000	34,000		1
		(11.5 ft)	(6-8ft)	(4-6ft)	2,100	(10-12ft)	(8-10ft)	(6-8ft)	(8-10ft)	(6-8ft)	(8-10ft)	(10-12ft)	(11.5ft)	(6-8ft)	2 1,000		
TOC- Groundwater	mg/L	1.0	1.4	1.4	1.3	6.5	9.3	14	14	15	12	10	22	25	14		1
Groundwater			-														—
Chloride	ma/I	21/21(1)	8.3/8.3 (1)	17	15	100	120	170	190	210	210	140	130	120	150		
	mg/L														150		
Nitrate	mg/L	1.8/1.8 ⁽¹⁾	2.4/2.4 (1)	1.7	2.0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5			
Sulfate	mg/L	130/130 ⁽¹⁾	120/120 (1)	240	163	0.7	1,200	430	4.4	2.3	1.6	4.7	0.9	< 0.5	180		
Bromide	mg/L	21/21(1)	<0.5/<0 .5 (1)	< 0.5	7.0	0.5	0.6	0.8	0.9	0.8	0.9	0.6	0.9	1.0	0.8		
pН	SU	5.04	4.76	4.05	4.6	6.09	5.93	6.17	6.38	6.27	6.35	6.42	6.42	6.39	6.27	7.24	8.80
•																(near 15)	
DO	mg/L	0.2	0.3	0.1	0.2	2.0	1.3	0.5	3.0	0.2	4.0	1.5	0.1	0.0	1.4	NT	NT
Conductivity	μS/cm	360	300	550	400	880	3,000	2,700	1,400	1,400	1,300	1,100	2,300	3,300	1,900	220	220
Temp	Celsius	17.4	16.2	16.9	17	17.1	16.8	15.8	18.1	18.3	17.3	17.6	17.0	16.5	17.2	25.2	25.6
ORP	mV	1.3	148	254	130	-168	-81	-235	-82	-90	-56	-132	-190	-206	-138	-55	55

ND-Not Detected

(1)-Duplicate

(2)-Confirmation by IC/MS/MS

NT-Not Tested

Perchlorate, Methane, TOC, Chloride, Nitrate, Sulfate, Bromide, DO, & Conductivity rounded to 2 significant figures.

					APPI	ENDIX (C - TABI	E C2					
				Sum	mary of	Laborat	ory Anal	ytical Re	esults				
Well ID			lorate	Chlorate	Chlorite	Chloride	Bromide	Nitrate	Nitrite	Sulfate	TOC	Phosphate	Methane
	Sample	Method 314	Method 332										
	Date	(μg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L) PIEZOMET	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(μg/L)
MW-1	2/5/02	85,000	NA	NA NA	NA NA	NA NA	NA NA	NA NA	NA NA	NA	NA	NA	NA
101 00 - 1	2/15/05	93,000	NA NA	NA	NA NA	16	NA	NA	113.0	38	NA NA	< 1	NA
	11/17/05	24,000	NA	NA	NA	16	< 1	140	< 0.5	41	2.2	< 1	<10
	9/28/06	15,000	NA	< 0.5	< 0.5	30	< 0.5	40	< 0.5	39	3.0	< 0.5	7.0
	4/17/08	18,000	23,000	< 0.5	< 0.5	29	< 0.5	26	< 0.5	35	1.7	NA	7.0
MW-2	2/5/02	1,900	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	2/15/05 11/17/05	3.0 16	NA NA	NA NA	NA NA	NA 1.8	NA < 1	NA 3.4	NA < 0.5	NA 63	NA 5.2	NA < 1	NA <10
	9/28/06	6.0	NA NA	< 0.5	< 0.5	2.1	< 0.5	1.3	< 0.5	44	5.1	< 0.5	<10 11
MW-3	2/5/02	1,600	NA NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	11/17/05	9,200	NA	NA	NA	4.7	< 1	0.8	< 0.5	57	2.4	< 1	<10
	9/28/06	11,000	NA	< 0.5	< 0.5	12	< 0.5	2.2	< 0.5	110	2.3	< 0.5	<4
	8/9/07	11,000	NA	< 0.5	< 0.5	14	< 0.5	2.3	< 0.5	83	1.3	NA	< 4
	4/17/08	4,100	NA	< 0.5	< 0.5	5.1	< 0.5	2.1	< 0.5	110	2.2	NA	<4
MW-4	2/5/02	180,000	NA	NA	NA	NA 11	NA	NA	NA 0.7	NA 120	NA	NA	NA
	2/15/05 11/17/05	36,000 26,000	NA NA	NA NA	NA NA	2.1	NA < 1	NA 1.6	8.7 < 0.5	57	NA 2.8	NA < 1	NA 42
	9/28/06	18,000	NA	< 0.5	< 0.5	8.1	< 0.5	1.2	< 0.5	110	4.7	< 0.5	27
	4/17/08	9,600	NA	< 0.5	< 0.5	9.4	< 0.5	3.5	< 0.5	51	2.5	NA	92
MW-5	2/5/02	83,000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	11/17/05	17,000	NA	NA	NA	2.3	<1	2.4	< 0.5	96	3.5	< 1	27
	9/28/06	2,300	NA	< 0.5	< 0.5	5.5	< 0.5	< 0.5	< 0.5	110	7.4	< 0.5	34
MW-6	4/17/08 2/5/02	8,800 142,000	8,600/9,000 NA	<0.5 NA	<0.5 NA	5.3 NA	<0.5 NA	6.5 NA	<0.5 NA	72 NA	2.7 NA	NA NA	6.0 NA
SGP-1S	11/17/05	2,600	NA NA	NA NA	NA NA	2.6	NA < 1	< 0.5	NA < 0.5	57	1.6	NA < 1	<10
BGI IB	9/27/06	2,400	2,800	< 0.5	< 0.5	5.5	< 0.5	0.8	< 0.5	90	1.8	< 0.5	5.0
	8/9/07	1,600	NA	< 0.5	< 0.5	5.8	< 0.5	< 0.5	< 0.5	90	2.1	NA	< 4
	4/15/08	3,300	NA	< 0.5	< 0.5	3.6	< 0.5	0.8	< 0.5	63	1.2	NA	8.0
SGP-1D	11/17/05	2,700	NA	NA	NA	5.2	< 1	0.9	< 0.5	80	1.8	< 1	<10
	9/27/06	2,200	NA	< 0.5	< 0.5	11	< 0.5	0.6	< 0.5	82	1.6	< 0.5	<4
	8/9/07 4/15/08	750 4,000	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	37 7.5	< 0.5 < 0.5	0.6 0.6	< 0.5	21 80	2.1 1.2	NA NA	< 4 7.0
SGP-2S	11/17/05	13,000	NA NA	< 0.5 NA	< 0.5 NA	11	< 0.5	0.8	< 0.5 < 0.5	130	1.2	NA < 1	59
561 25	9/26/06	16,000	NA	< 0.5	< 0.5	12	< 0.5	1.9	< 0.5	150	1.6	< 0.5	21
	8/9/07	13,000	NA	< 0.5	< 0.5	14	< 0.5	2.4	< 0.5	170	1.5	NA	< 4
	4/15/08	11,000	NA	< 0.5	< 0.5	17	< 0.5	1.6	< 0.5	97	1.1	NA	10
SGP-2D	11/17/05	12,000	NA	NA	NA	9.7	< 1	<0.5	< 0.5	78	8.0	< 1	23
	9/26/06	33,000	NA	< 0.5	< 0.5	18	< 0.5	3.7	< 0.5	140	1.5	< 0.5	7.0
	3/28/07 8/9/07	4,500 15,000	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	6.9 19	< 0.5 < 0.5	3.9 1.9	< 0.5 < 0.5	130 97	NA 1.4	< 0.5 NA	NA 80
	4/15/08	10,000	NA NA	< 0.5	< 0.5	13	< 0.5	2.9	< 0.5	130	1.4	NA NA	9.0
SGP-3S	11/17/05	23	NA	NA	NA	4.8	< 1	< 0.5	< 0.5	55	1.3	< 1	<10
	9/26/06	46	NA	< 0.5	< 0.5	12	< 0.5	1.1	< 0.5	89	1.4	< 0.5	17
	8/9/07	19	NA	< 0.5	< 0.5	10	< 0.5	< 0.5	< 0.5	68	6.2	NA	< 4
200 AD	4/15/08	11	NA	<0.5	<0.5	16	<0.5	<0.5	<0.5	71	1.8	NA	<4
SGP-3D	11/17/05 9/26/06	80 89	NA NA	NA < 0.5	NA < 0.5	2.3 13	< 1 < 0.5	< 0.5 1.9	< 0.5 < 0.5	60 160	< 1	< 1 < 0.5	<10 7.0
	8/9/07	48	NA NA	< 0.5 < 0.5	< 0.5	3.9	< 0.5	< 0.5	< 0.5	57	1.6 2.2	< 0.5 NA	7.0 < 4
	4/15/08	210	NA NA	<0.5	<0.5	8.7	<0.5	1.00	<0.5	84	1.0	NA	6.0
SGP-4S	11/17/05	346	NA	NA	NA	6.4	< 1	6.0	<0.5	16	15	< 1	<10
	9/27/06	317	NA	< 0.5	< 0.5	2.6	< 0.5	2.0	< 0.5	31	3.0	< 0.5	36
	4/17/08	56	NA	< 0.5	< 0.5	1.2	< 0.5	2.1	< 0.5	25	2.9	NA	48
SGP-4D	11/17/05	5,700	NA	NA	NA	2.6	< 1	1.4	< 0.5	47	2.2	< 1	<10
	9/27/06	5,800	NA NA	< 0.5	< 0.5	5.7	< 0.5	13	< 0.5	68	2.0	< 0.5	31
	4/17/08	2,400	NA	< 0.5	< 0.5	4.1	< 0.5	9.9	< 0.5	61	1.8	NA	7.0

					APPI	ENDIX (C - TABI	E C2					
				Sum	mary of	Laborat	ory Anal	ytical Re	esults				
Well ID			lorate	Chlorate	Chlorite	Chloride	Bromide	Nitrate	Nitrite	Sulfate	TOC	Phosphate	Methane
	Sample	Method 314	Method 332										
	Date	(μg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(μg/L)
SGP-5S	11/17/05 9/28/06	230 15	NA	NA < 0.5	NA <0.5	5.3 7.3	< 1 < 0.5	1.1	< 0.5 < 0.5	100 150	2.6 2.4	< 1 < 0.5	<10 <4
	9/28/06 4/17/08	48	NA NA	< 0.5	<0.5 <0.5	4.9	< 0.5	2.8 3.5	< 0.5	120	1.1	< 0.5 NA	<4 <4
SGP-5D	11/17/05	320	NA NA	NA	NA	4.9	< 0.3	2.0	< 0.5	170	1.5	< 1	<10
561 55	9/28/06	480	NA	< 0.5	< 0.5	25	< 0.5	8.0	< 0.5	310	1.2	< 0.5	<4
	4/17/08	210	NA	< 0.5	< 0.5	11	< 0.5	0.8	< 0.5	150	1.2	NA	18
SGP-6S	11/17/05	18,000	NA	NA	NA	11	< 1	2.8	< 0.5	110	3.1	< 1	83
	9/28/06	10,000	NA	< 0.5	< 0.5	22	< 0.5	0.6	< 0.5	150	< 1	< 0.5	46
	4/17/08	4,500	NA	< 0.5	< 0.5	17	< 0.5	< 0.5	< 0.5	110	1.6	NA	16
SGP-6D	11/17/05	17,000	NA	NA	NA	11	< 1	< 0.5	< 0.5	77	29	< 1	1,100
	9/28/06	< 1	NA	< 0.5	< 0.5	25	< 0.5	< 0.5	< 0.5	< 0.5	32	< 0.5	7,100
	3/29/07	< 1	NA	< 0.5	< 0.5	26	< 0.5	< 0.5	< 0.5	9	NA	<50	NA
	4/17/08	<1	NA	< 0.5	< 0.5	26	< 0.5	< 0.5	< 0.5	6	24	NA	1,100
SGP-7S	11/17/05	40	NA	NA	NA	3.8	< 1	2.6	< 0.5	62	3.5	< 1	<10
	9/28/06 4/17/08	59	NA	< 0.5	< 0.5	7.3	< 0.5	1.6	< 0.5	72	2.9 3.2	< 0.5	<4
SGP-7D	11/17/05	520 41	NA NA	< 0.5 NA	< 0.5 NA	2.4 4.4	< 0.5 < 1	< 0.5	< 0.5	63 80	9.2	NA < 1	<4 <10
SGP-/D	9/28/06	150	NA NA	< 0.5	< 0.5	7.8	< 0.5	1.9	< 0.5	98	1.7	< 0.5	14
	4/17/08	390	NA NA	< 0.5	< 0.5	2.8	< 0.5	3.1	< 0.5	98	1.7	NA	17
SGP-8S	11/17/05	28,000	NA	NA	NA NA	15	< 1	7.7	< 0.5	78	2.1	<1	11
	9/28/06	14,000	NA	< 0.5	< 0.5	29	< 0.5	22	< 0.5	75	< 1	< 0.5	21
	4/17/08	12,000	NA	< 0.5	< 0.5	32	< 0.5	22	< 0.5	55	2.0	NA	250
SGP-8D	11/17/05	27,000	NA	NA	NA	10	<1	4.9	< 0.5	63	3.4	<1	<10
	9/28/06	<1	NA	< 0.5	< 0.5	12	< 0.5	< 0.5	< 0.5	18	5.2	< 0.5	301
	3/29/07	<1	NA	< 0.5	< 0.5	16	< 0.5	< 0.5	< 0.5	30	NA	< 50	NA
	4/17/08	11	NA	< 0.5	< 0.5	22	< 0.5	< 0.5	< 0.5	29	4.5	NA	<4
TP-5	3/29/07	1,800	NA	< 0.5	< 0.5	33	< 0.5	0.6	< 0.5	120	NA	< 50	NA
	8/8/07	1,300	NA	< 0.5	< 0.5	102	< 0.5	< 0.5	< 0.5	80	2.9	NA	13
mm o	4/16/08	1,300	NA	< 0.5	< 0.5	126	< 0.5	< 0.5	< 0.5	83	2.5	NA	150
TP-8	3/30/07	34,000	NA	< 0.5	< 0.5	32 28	< 0.5	< 0.5	< 0.5	450	NA	< 50	NA
	4/16/08	22,000	NA	< 0.5	< 0.5		< 0.5 ETERS IN	< 0.5	< 0.5	330	2.4	NA	130
SGP-9	6/7/06	200	NA	< 0.5	< 0.5	21	< 0.5	1.8	< 0.5	130	< 1	< 10	<4
3GP-9	9/27/06	61	75	< 0.5	< 0.5	24	< 0.5	0.5	< 0.5	100	1.1	< 0.5	78
	8/9/07	< 1	NA	< 0.5	< 0.5	23	< 0.5	< 0.5	< 0.5	48	2.8	NA	240
	4/16/08	130	NA	< 0.5	< 0.5	18	< 0.5	1.0	< 0.5	110	0.9	NA	20
SGP-19	6/7/06	4,400	NA	< 0.5	< 0.5	8.3	< 0.5	2.4	< 0.5	120	1.4	<10	<4
	9/27/06	4,200	NA	< 0.5	< 0.5	8.2	< 0.5	2.0	< 0.5	120	1.6	< 0.5	<4
	3/29/07	3,400	NA	< 0.5	< 0.5	5.5	< 0.5	2.9	< 0.5	130	NA	< 50	NA
	8/8/07	4,200	NA	< 0.5	< 0.5	7.4	< 0.5	2.3	< 0.5	110	1.1	NA	< 4
	4/16/08	4,700	NA	< 0.5	< 0.5	6.2	< 0.5	2.7	< 0.5	110	1.2	NA	<4
SGP-20	6/7/06	13,000	NA	< 0.5	< 0.5	17	< 0.5	1.7	< 0.5	240	1.4	< 10	115
	9/27/06	11,000	NA	< 0.5	< 0.5	13	< 0.5	< 0.5	< 0.5	280	1.6	< 0.5	136
	3/30/07	10,000	NA	< 0.5	< 0.5	14	< 0.5	< 0.5	< 0.5	270	NA	< 50	NA
	8/9/07 4/16/08	1,700	NA NA	< 0.5	< 0.5	17	< 0.5	< 0.5	< 0.5	300	2.1	NA NA	73 120
SGP-21	9/27/06	10,000	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	14 110	< 0.5 < 0.5	< 0.5 < 0.5	< 0.5 < 0.5	250 33	1.6 7.7	NA < 0.5	4,400
5Gr-21	3/29/07	< 1	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	100	< 0.5 < 0.5	< 0.5 < 0.5	< 0.5 < 0.5	33 75	7.7 NA	< 0.5 < 50	4,400 NA
	8/9/07	< 1	NA <1	< 0.5	< 0.5	48	< 0.5	< 0.5	< 0.5	35	2.7	NA	71
	4/17/08	<1	NA	< 0.5	< 0.5	95	< 0.5	< 0.5	< 0.5	57	8.0	NA NA	120
DP-1	3/30/07	3,500	NA NA	< 0.5	< 0.5	9.0	< 0.5	< 0.5	< 0.5	57	NA	< 50	NA
DP-3	3/29/07	21,000	NA	< 0.5	< 0.5	42	< 0.5	< 0.5	< 0.5	530	NA	< 50	NA

					APPI	ENDIX (C - TABL	E C2					
				Sum	mary of	Laborate	ory Anal	ytical Re	esults				
Well ID			lorate	Chlorate	Chlorite	Chloride	Bromide	Nitrate	Nitrite	Sulfate	TOC	Phosphate	Methane
	Sample	Method 314	Method 332	(/T)	(/r)	(/T)	(/T)	(m)	(m)	(/T)	(M)	((. m)
	Date	(μg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L) EZOMETER	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(μg/L)
A TP-1	3/29/07	< 1	NA	< 0.5	< 0.5	95	< 0.5	< 0.5	< 0.5	2.1	NA	< 50	NA
shallow	8/9/07	< 1	0.1	< 0.5	< 0.5	93	< 0.5	< 0.5	< 0.5	< 0.5	5.3	NA	810
	4/16/08	<4	< 0.02	< 0.5	< 0.5	64	< 0.5	< 0.5	< 0.5	< 0.5	4.9	NA	2,000
B TP-2	3/29/07	5.9	NA	< 0.5	< 0.5	42	< 0.5	< 0.5	< 0.5	42	NA	< 50	NA
intermediate	8/9/07	< 1	NA	< 0.5	< 0.5	49	< 0.5	< 0.5	< 0.5	9.3	0.2	NA	360
	4/16/08	<1	***	< 0.5	< 0.5	44	< 0.5	< 0.5	< 0.5	13	4.3	NA	640
C TP-3 deep	3/29/07 8/9/07	2,700 2,400	NA NA	< 0.5 < 0.5	<0.5 < 0.5	16 6.4	< 0.5 < 0.5	0.5 < 0.5	< 0.5 < 0.5	110 68	NA 1.0	< 50 NA	NA 53
аеер	4/16/08	3,200	NA NA	< 0.5	< 0.5	12	< 0.5	0.5	< 0.5	110	1.0	NA NA	150
Column 3 (IC-3)	8/8/07	< 1	0.06	< 0.5	< 0.5	290	0.9	< 0.5	< 0.5	55	6.2	NA NA	1,600
	12/18/07	< 1	NA	< 0.5	< 0.5	450	1.4	< 0.5	< 0.5	81	NA	NA	NA
	4/15/08	<1	NA	< 0.5	< 0.5	220	0.8	< 0.5	< 0.5	39	6.8	NA	<4
Column 4 (IC-4)	8/8/07	< 1	NA	< 0.5	< 0.5	200	0.6	< 0.5	< 0.5	39	6.5	NA	< 4
	12/18/07	< 1	NA	< 0.5	< 0.5	560	1.7	1.1	< 0.5	110	NA	NA	NA
	4/16/08	<4	NA	< 0.5	<0.5	30	<0.5	1.1	< 0.5	15	4.7	NA	<4
A TP-4	3/30/07	6.7	NA	< 0.5	< 0.5	55	< 0.5	< 0.5	< 0.5	27	NA	< 50	NA
shallow	8/9/07	< 1	NA NA	< 0.5	< 0.5	62	< 0.5	0.6	< 0.5	1.4	3.9	NA	450
shanow	4/16/08	<1	0.61	< 0.5	< 0.5	56	< 0.5	<0.5	< 0.5	2.2	5.9	NA NA	400
B TP-6	3/30/07	3.4	NA	< 0.5	< 0.5	35	< 0.5	< 0.5	< 0.5	150	NA	< 50	NA
intermediate	8/9/07	< 1	NA	< 0.5	< 0.5	29	< 0.5	< 0.5	< 0.5	96	1.5	NA	230
	4/16/08	<1	NA	< 0.5	< 0.5	36	< 0.5	< 0.5	< 0.5	84	2.4	NA	400
C TP-7	3/30/07	3,200	NA	< 0.5	< 0.5	27	< 0.5	< 0.5	< 0.5	210	NA	< 50	NA
deep	8/9/07	640	NA	< 0.5	< 0.5	29	< 0.5	< 0.5	< 0.5	220	2.5	NA	17
D DP-2	4/16/08 3/30/07	3,300 3,700	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	6.2	< 0.5 < 0.5	< 0.5 < 0.5	< 0.5 < 0.5	210 75	1.6 NA	NA < 50	25 NA
Column 1 (IC-1)	8/9/07	< 1	NA NA	< 0.5	< 0.5	360	1.0	< 0.5	< 0.5	54	6.6	NA	91
Column 1 (IC 1)	12/18/07	< 1	NA	< 0.5	< 0.5	560	1.9	2.3	< 0.5	110	NA	NA	NA
	4/15/08	<4	NA	< 0.5	< 0.5	33	< 0.5	1.1	< 0.5	18	5.9	NA	<4
Column 2 (IC-2)	8/9/07	< 1	NA	< 0.5	< 0.5	360	1.2	< 0.5	< 0.5	70	6.8	NA	110
	12/18/07	< 1	NA	< 0.5	< 0.5	630	2.4	2.7	< 0.5	110	NA	NA	NA
	4/16/08	< 1	NA	< 0.5	< 0.5	62	< 0.5	0.6	< 0.5	18	4.8	NA	2,700
200 220	0.000.00						TERS IN TE				1 40	1 0.5	
SGP-22S	9/27/06 8/8/07	< 1 < 1	0.08 NA	< 0.5 < 0.5	< 0.5 < 0.5	120 110	0.6 < 0.5	< 0.5 0.6	< 0.5 < 0.5	89 100	12 1.1	< 0.5 NA	6,300 2,900
	4/16/08	<1	NA NA	< 0.5	< 0.5	110	0.6	0.6	< 0.5	100	1.1	NA NA	4,500
SGP-22D	9/27/06	<1	0.05	< 0.5	< 0.5	98	0.5	< 0.5	< 0.5	1,700	6.6	< 0.5	49
i l	8/8/07	< 1	NA	< 0.5	< 0.5	77	< 0.5	< 0.5	< 0.5	2,000	0.1	NA	12
	4/16/08	<1	NA	< 0.5	< 0.5	97	0.5	< 0.5	< 0.5	1,900	4.9	NA	25
SGP-22SW	9/27/06	< 1	NA	< 0.5	< 0.5	130	< 0.5	0.5	< 0.5	36	5.1	< 0.5	<4
i l	8/8/07	< 4	NA	< 0.5	< 0.5	360	1.5	< 0.5	< 0.5	72	8.4	NA	< 4
SGP-23S	4/16/08 9/27/06	61 < 1	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	30 130	<0.5 0.5	1.3 < 0.5	< 0.5 < 0.5	22 41	4.7 9.8	NA < 0.5	5.0 4,000
SGF-23S	9/27/06 4/16/08	<1 <1	NA NA	< 0.5 < 0.5	< 0.5	100	0.5	< 0.5	< 0.5 < 0.5	<0.5	9.8	< 0.5 NA	4,000 9,400
SGP-23D	9/27/06	<1	NA NA	< 0.5	< 0.5	110	< 0.5	< 0.5	< 0.5	15	4.4	< 0.5	1,100
	8/8/07	< 1	NA	< 0.5	< 0.5	84	< 0.5	< 0.5	< 0.5	2.0	4.3	NA	1,200
<u> </u>	4/16/08	<1	NA	< 0.5	< 0.5	100	< 0.5	< 0.5	< 0.5	< 0.5	4.4	NA	630
SGP-23SW	9/27/06	<1	NA	< 0.5	< 0.5	130	< 0.5	0.7	< 0.5	35	4.7	< 0.5	<4
SGP-24S	9/27/06	< 1	NA	< 0.5	< 0.5	99	< 0.5	< 0.5	< 0.5	9.7	10	< 0.5	13,000
i l	8/8/07	< 1	NA	< 0.5	< 0.5	100	< 0.5	< 0.5	< 0.5	< 0.5	6.5	NA	6,500
SGP-24D	4/16/08	<1	NA NA	< 0.5 < 0.5	< 0.5 < 0.5	130 100	0.60 < 0.5	< 0.5 < 0.5	< 0.5	0.5 9.5	9.6	NA < 0.5	19,000 12,000
5Gr-24D	9/27/06 8/8/07	< 1 < 1	NA NA	< 0.5 < 0.5	< 0.5	32	< 0.5 < 0.5	< 0.5	< 0.5 < 0.5	9.5 < 0.5	9.6 3.9	< 0.5 NA	12,000 4,400
	4/16/08	<1 <1	NA NA	< 0.5	< 0.5	100	0.50	< 0.5	< 0.5	< 0.5	4.7	NA NA	12,000/11,000
SGP-24SW	9/27/06	<1	NA	< 0.5	< 0.5	130	< 0.5	1.20	< 0.5	36	4.5	< 0.5	<4

	APPENDIX C - TABLE C2 Summary of Laboratory Analytical Results												
				Sum	mary of	Laborate	ory Anal	ytical Re	esults				
Well ID			lorate	Chlorate	Chlorite	Chloride	Bromide	Nitrate	Nitrite	Sulfate	TOC	Phosphate	Methane
	Sample	Method 314	Method 332										
	Date	(μg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(μg/L)
				NITOR WE	LLS AND I	PIEZOMET	ERS IN TH	E SUBTIDA	L SHALLO				
SGP-10	6/7/06	< 1	NA	< 0.5	< 0.5	100	0.5	< 0.5	< 0.5	0.7	6.5	< 10	6,300
	9/26/06	< 1	NA	< 0.5	< 0.5	140	0.6	< 0.5	< 0.5	< 0.5	7.4	< 0.5	13,000
SGP-11	6/7/06	< 1	NA	< 0.5	< 0.5	120	0.6	< 0.5	< 0.5	1,200	9.3	< 10	10
	9/26/06	< 1	NA	< 0.5	< 0.5	62	< 0.5	< 0.5	< 0.5	720	10	< 0.5	38
SGP-12	6/7/06	< 1	NA	< 0.5	< 0.5	170	0.8	< 0.5	< 0.5	430	14	< 10	1,300
	9/26/06	< 1	NA	< 0.5	< 0.5	190	1.0	< 0.5	< 0.5	470	14	2.40	2,900
SGP-13	6/7/06	< 1	NA	< 0.5	< 0.5	190	0.9	< 0.5	< 0.5	4.4	14	< 10	8,400
	9/26/06	< 1	NA	< 0.5	< 0.5	230	1.1	2.20	0.90	2.5	14	< 0.5	16,000
SGP-14	6/7/06	< 1	NA	< 0.5	< 0.5	210	0.8	< 0.5	< 0.5	2.3	15	< 10	6,200
	9/26/06	< 1	NA	< 0.5	< 0.5	260	1.1	1.30	< 0.5	4.9	16	< 0.5	14,000
SGP-15	6/7/06	< 1	NA	< 0.5	< 0.5	210	0.9	< 0.5	< 0.5	1.6	12	< 10	4,300
	9/26/06	< 1	NA	< 0.5	< 0.5	240	1.1	< 0.5	< 0.5	12	13	< 0.5	9,700
SGP-16	6/7/06	< 1	NA	< 0.5	< 0.5	140	0.6	< 0.5	< 0.5	4.7	10	< 10	12,000
	9/26/06	< 1	NA	< 0.5	< 0.5	190	0.9	< 0.5	< 0.5	< 0.5	13	< 0.5	16,000
SGP-17	6/7/06	< 1	NA	< 0.5	< 0.5	130	0.9	< 0.5	< 0.5	0.9	22	< 10	12,000
	9/26/06	< 1	NA	< 0.5	< 0.5	180	1.5	< 0.5	< 0.5	< 0.5	32	< 0.5	19,000
SGP-18	6/7/06	< 1	NA	< 0.5	< 0.5	120	1.0	< 0.5	< 0.5	< 0.5	25	< 10	13,000
	9/26/06	< 1	NA	< 0.5	< 0.5	150	1.2	< 0.5	< 0.5	< 0.5	35	< 0.5	12,000
					SUF	RFACE WA	TER SAMP	LES					
SW-1	3/29/07	< 4	NA	< 0.5	< 0.5	32	< 0.5	< 0.5	< 0.5	56	NA	< 50	NA
	12/18/07	< 1	NA	< 0.5	< 0.5	380	1.3	< 0.5	< 0.5	65	NA	NA	NA
SW-2	3/29/07	< 1	NA	< 0.5	< 0.5	37	< 0.5	< 0.5	< 0.5	15	NA	< 50	NA
	12/18/07	8.7	NA	< 0.5	< 0.5	340	1.3	< 0.5	< 0.5	64	NA	NA	NA
SW-3	3/29/07	< 1	NA	< 0.5	< 0.5	32	< 0.5	< 0.5	< 0.5	16	NA	< 50	NA
SW-4	3/29/07	< 1	NA	< 0.5	< 0.5	27	< 0.5	1.1	< 0.5	18	NA	< 50	NA
SEEP-1	3/29/07	< 1	NA	< 0.5	< 0.5	43	< 0.5	< 0.5	< 0.5	2.0	NA	< 50	NA

Notes:

Notes.

NA denotes not analyzed.

February 2002 data taken from Cramer & Yates, 2004

APPENDIX C - TABLE C3 Summary of Natural Attenuation Parameters											
Well ID	Sample	pН	DO	Conductivity	Temp.	ORP	Turbidity	Manganese	Iron		
	Date	SU	(mg/L)	(µS/cm)	°C	mv (1)	NTU	(mg/L)	(mg/L)		
MONITOR WELLS AND PIEZOMETERS ON LAND											
MW-1	11/15/05	5.46	0.2	498	19.1	NR	NS	NS	NS		
	9/28/06	5.74	1.0	374	22.8	62	7	0	0		
	4/17/08	6.12	0.5	295	14.1	127	NS	0	0		
MW-2	11/15/05	7.14	0.5	540	17.0	NR	NS	NS	NS		
	9/28/06	6.73	1.0	528	20.2	22	15	0	0		
	4/17/08	NS	NS	NS	NS	NS	NS	NS	NS		
MW-3	11/15/05	3.81	2-3	322	17.7	NR	NS	NS	NS		
	9/28/06	4.42	0.5	317	19.7	26	37	0	0		
	8/9/07	4.72	NS	256	26.6	193	NS	NS	NS		
	4/17/08	5.19	0.5	392	12.0	89	NS	0	0		
MW-4	11/15/05	4.96	0.1	382	18.4	NR	NS	NS	NS		
	9/28/06	5.66	1.0	416	20.8	40	16	0	0		
CPMW-5	4/17/08 11/15/05	5.95 3.79	0.4	294 458	12.8 18.5	101 NR	NS NS	0 NS	0 NS		
CFWIW-3	9/28/06	6.30	1.0	456	21.6	26	18	0	0		
	4/17/08	6.46	0.4	361	13.8	48	NS	0	0		
SGP-1S	11/16/05	4.92	2-3	281	16.2	NR	NS	NS	NS		
561 15	9/27/06	4.76	1.5	268	18.3	-58	9	0	0		
	8/9/07	5.02	NS	211	20.6	183	NS	NS	NS		
	4/16/08	4.88	0.4	222	11.9	84	NS	0	0		
SGP-1D	11/16/05	5.39	4.0	320	16.2	NR	NS	NS	NS		
	9/27/06	4.44	2.0	216	17.9	-66	72	0	0		
	8/9/07	4.55	NS	166	19.2	187	NS	NS	NS		
	4/16/08	4.88	1.0	169	12.5	86	NS	0	5		
SGP-2S	11/16/05	4.65	1.0	448	16.8	NR	NS	NS	NS		
	9/26/06	4.56	3.5	389	17.5	251	178	0	0		
	8/9/07	4.29	NS	368	20.0	192	NS	NS	NS		
	4/16/08	4.39	0.3	355	12.6	102	NS	0	0		
SGP-2D	11/16/05	4.81	NS	392	16.4	NR	NS	NS	NS		
	9/26/06	4.91	7.0	423	16.7	204	94	0	4		
	3/28/07	5.32	NS	364	15.9	NS	NS	NS	NS		
	8/907	4.96	NS	347	20.4	173 91	NS	NS	NS		
SGP-3S	4/16/08 11/17/05	5.05 5.46	0.8 5 - 6	375 264	12.8 17.4	NR	NS NS	0 NS	0 NS		
3GF-33	9/26/06	5.23	2.0	269	18.0	129	28	0	0		
	8/9/07	4.90	NS NS	198	20.0	175	NS NS	NS	NS		
	4/15/08	4.96	1.0	254	12.4	53	NS	0	2		
SGP-3D	11/16/05	4.30	5 - 6	359	16.5	NR	NS	NS	NS		
	9/26/06	3.91	2.5	400	16.9	320	14	0	0		
	8/9/07	4.12	NS	214	21.2	184	NS	NS	NS		
	4/16/08	4.01	1.0	350	11.5	104	NS	0.5	0		
SGP-4S	11/17/05	10.75	7.0	1150	14.4	NR	NS	NS	NS		
	9/27/06	6.24	2.5	424	18.6	-74	868	0	38.0		
	4/17/08	6.79	1.0	376	11.2	17	NS	0	0		
SGP-4D	11/17/05	7.78	8 - 10	410	14.8	NR	NS	NS	NS		
	9/27/06	5.47	1.0	298	17.1	-80	12	0	0		
	4/17/08	5.47	1.0	234	11.8	78	NS	0	5		
SGP-5S	11/17/05	5.43	7.0	406	14.6	NR	NS	NS	NS		
	9/28/06	4.41	1.0	336	16.9	12	61	0	0		
	4/17/08	4.44	0.8	311	10.0	110	NS	0	0		
SGP-5D	11/16/05	3.71	2.0	584	16.4	NR	NS	NS	NS		
	9/28/06	3.66	1.5	589	16.1	23	12	0	9		
	4/17/08	4.46	0.5	368	11.3	98	NS	0.3	5		

APPENDIX C - TABLE C3 Summary of Natural Attenuation Parameters									
Well ID	Sample	pН	DO	Conductivity (µS/cm)	Temp.	ORP my (1)	Turbidity	Manganese	Iron
GGD CG	Date	SU	(mg/L)				NTU	(mg/L)	(mg/L)
SGP-6S	11/17/05	6.62	5.0	687	16.5	NR	NS 84	NS	NS
	9/28/06 4/17/08	4.75 5.23	1.0	417 413	21.3 13.6	13 89	84 NS	0	0
SCD (D									
SGP-6D	11/17/05	6.35	2-3	642	16.9	NR	NS	NS	NS
	9/28/06	6.37	0.5	697	20.9	-77	NS	0	54
	3/29/07	6.47	NS 7.0	447	15.6	43	NS NG	NS	NS 20
CCD 7C	4/17/08 11/16/05	6.35	4 - 5	528	12.3	18 ND	NS NG	0 NS	30
SGP-7S		5.49		342	18.2	NR	NS		NS
	9/28/06	5.66	1.0	329	19.3	11	NS	0	0
aan an	4/17/08	6.27	1.0	382	12.5	44	NS	0	5
SGP-7D	11/16/05	3.96	3-4	374	18.4	NR	NS	NS	NS
	9/28/06	4.03	2.5	257	19.2	26	>1000	0	4.0
	4/17/08	4.74	1.5	221	15.4	152	NS	0	0
SGP-8S	11/17/05	4.69	2-3	366	17.3	NR	NS	NS	NS
	9/28/06	4.01	1.5	337	21.7	113	65	0	0
	4/17/08	4.41	4.0	376	12.9	163	NS	0	5
SGP-8D	11/17/05	6.28	2.0	386	16.7	NR	NS	NS	NS
	9/28/06	6.11	2.0	281	19.9	-10	521	0	2
	3/29/07	6.75	NS	283	15.5	45	NS	NS	NS
	4/17/08	6.24	4.0	277	13.5	50	NS	0	30
•			MONITO	R WELLS IN T	HE LITTO	ORAL ZO	NE		•
SGP-9	6/7/06	5.04	0.2	357	17.3	1	NS	NS	NS
	9/27/06	5.12	1.5	364	22.3	59	5	0	0
	8/9/2007	5.37	NS	257	24.3	84	NS	NS	NS
	4/16/08	4.90	0.6	364	13.3	48	NS	0.6	5
SGP-19	6/7/06	4.76	0.3	303	16.2	148	NS	0.0	
301-17	9/27/06	4.50	3.5	326	20.7	60	9	0	0
	8/8/07	4.86	NS NS	315	33.8	117	NS	NS	NS
	4/16/08	4.89	0.2	298	13.8	13	NS NS	0.3	5
SGP-20			0.2	545	16.9	254	NS NS	0.3	3
3GF-20	6/7/06	4.05						0	0
	9/27/06	3.86	1.5	599	20.9	109	16	0	0
	8/9/07	4.28	NS	521	23.8	173	NS	NS	NS
aan M	4/16/08	4.25	0.3	558	13.1	48	NS	0	5
SGP-21	9/27/06	6.14	1.5	776	21.5	-85	83	0	60
	8/9/07	6.09	NS	746	22.3	-48	NS	NS	NS
	4/17/08	6.22	0.1	794	13.1	1	NS	0.00	90
TP-1	8/9/07	6.06	NS	420	28.2	50	NS	NS	NS
	4/16/08	6.50	2.0	389	16.3	-59	NS	0.30	5
TP-2	8/9/07	5.93	NS	327	25.6	37	NS	NS	NS
	4/16/08	6.39	1.0	306	15.8	-24	NS	0.00	15
TP-3	8/9/07	5.04	NS	293	25.9	151	NS	NS	NS
	4/16/08	4.62	1.0	288	16.7	45	NS	0.00	8
TP-4	8/9/07	6.11	NS	409	24.9	-8	NS	NS	NS
	4/16/08	6.68	1.0	403	16.5	-9	NS	0.00	8
TP-5	8/8/07	5.24	NS	524	27.3	96	NS	NS	NS
	4/16/08	5.98	1.0	742	14.4	-31	NS	0.00	20
TP-6	8/9/07	5.78	NS	482	23.8	22	NS	NS	NS
	4/16/08	6.24	1.0	434	15.3	1	NS	0.30	5
TP-7	8/9/07	5.38	NS	532	25.5	111	NS	NS	NS
	4/16/08	4.84	0.8	527	15.5	52	NS	0.60	15
TP-8	4/16/08	3.98	0.6	898	12.6	132	NS	0.3	30
olumn 1 (IC-1)	8/9/07	6.87	NS	1,280	29.5	-45	NS	NS	NS
(10 1)	4/15/08	7.27	7.0	250	19.4	-45	NS	0	0
olumn 2 (IC-2)	8/9/07	6.75	NS	1,250	28.9	-42	NS	NS	NS
J. (1C-2)	4/16/08	6.68	1.0	235	18.4	12	NS	0	0
olumn 3 (IC-3)	8/8/07	6.30	NS	926	35.4	-30	NS	NS	NS
ommin 3 (IC-3)									
olumn 4 GC A	4/16/08	6.53	NS	1,078	15.3	-49 52	NS NC	NS	NS NC
olumn 4 (IC-4)	8/8/07	6.68	NS 2.0	1,097	34.1	-52	NS NG	NS	NS
	04/16/08	6.43	2.0	247	17.2	-34	NS	0	5

APPENDIX C - TABLE C3 Summary of Natural Attenuation Parameters										
Well ID	Sample Date	pH SU	DO (mg/L)	Conductivity (µS/cm)	Temp.	ORP mv (1)	Turbidity NTU	Manganese (mg/L)	Iron (mg/L)	
SUBTIDAL CHANNEL MONITOR WELLS										
SGP-22S	9/27/06	5.93	1.5	1,460	22.4	-56	7	0	30	
	8/8/07	6.02	1.5	1,410	26.3	-36	NS	0	25	
	4/16/08	6.25	0.5	1,510	12.6	-4	NS	0	45	
SGP-22D	9/27/06	5.51	4.5	3,280	20.9	6	6	0	390	
	8/8/07	5.59	1.5	2,780	23.8	12	NS	0	> 300	
	4/16/08	3.41	1.0	2,930	13.8	383	NS	0.8	175	
SGP-22SW	9/27/06	9.03 6.50	11.0 8.0	607 1,380	26.5 28.9	-29 -3	14 NS	0	0	
(sws-1)	8/8/07 4/16/08	7.29	5.0	251	19.7	-3 54	NS NS	0	5	
SGP-23S	9/27/06	6.69	4.5	943	23.8	-12	NS	0	23	
501 255	4/16/08	6.66	0.8	891	15.9	-77	NS	0	90	
SGP-23D	9/27/06	5.95	5.0	633	21.0	6	NS	0	30	
	8/8/07	6.30	3.5	680	23.8	-83	NS	0	> 300	
	4/16/08	6.70	0.8	542	14.3	-29	NS	0.6	45	
SGP-23SW	9/27/06	8.41	11.0	618	25.4	-44	NS	0	23	
(sws-2)	4/16/08	NS	NS	NS	NS	NS	NS	NS	NS	
SGP-24S	9/27/06	6.34	1.0	932	22.6	-107	18	0	45	
	8/8/07	6.45	2.5	866	29.5	-115	NS	0	> 300	
CCD A4D	4/16/08 9/27/06	6.54	1.5	1,020 903	13.5	-76	NS 19	0	45	
SGP-24D	8/8/07	6.28	2.5	903 646	21.3	-89 -8	18 NS	0	300	
	4/16/08	6.36	0.8	705	13.7	-80	NS NS	0.6	5	
SGP-24SW	9/27/06	6.34	6.5	932	22.6	-57	8	0.0	45	
(sws-3)	4/16/08	NS NS	NS	NS	NS NS	NS	NS	NS	NS	
(== 5)	5/ 00	- 10		AL SHALLOWS					- 10	
SGP-10	6/7/06	6.09	2.0	883	17.1	-168	NS			
	9/26/06	6.05	2.0	794	20.5	-57	61	0	9	
SGP-11	6/7/06	5.93	1.3	2,990	16.8	-81	NS			
	9/26/06	5.94	5.0	2,190	21.8	-83	43	0	120	
00D 12	c/=/0 c		0.7	2.520	4.50	22.1	170			
SGP-12	6/7/06 9/26/06	6.17	0.5 1.5	2,730 1,480	15.8 18.6	-234 -226	NS 4	0	0	
	9/20/00	0.22	1.5	1,480	18.0	-220	4	U	0	
SGP-13	6/7/06	6.38	3.0	1,420	18.1	-82	NS			
	9/26/06	6.40	1.5	1,030	19.2	-130	116	0	12	
				,						
SGP-14	6/7/06	6.27	0.2	1,390	18.3	-90	NS			
	9/26/06	6.30	2.5	1,120	20.2	-151	351	0	60	
			1							
SGP-15	6/7/06	6.35	4.0	1,310	17.3	-56	NS			
	9/26/06	6.34	1.5	1,080	20.3	-96	NS	0	15	
	<u> </u>						 			
SGP-16	6/7/06	6.42	1.5	1,130	17.6	-132	NS			
501-10	9/26/06	6.42	2.5	1,140	20.7	-132	72	0	30	
	2.2000	3.12	2.0	-,1.0		/	 			
SGP-17	6/7/06	6.42	0.1	2,330	17.0	-190	NS			
	9/26/06	6.46	1.5	2,390	20.3	-139	26	0	60	
			 				 			
SGP-18	6/7/06	6.39	0.0	3,260	16.5	-206	NS			
SGP-18	6/7/06 9/26/06	6.39 6.47	0.0	3,260 3,460	16.5 20.6	-206 -147	NS 32	0	60	

NR = Not Reported because ORP meter was not working correctly during Nov 05.

NA denotes not analyzed.

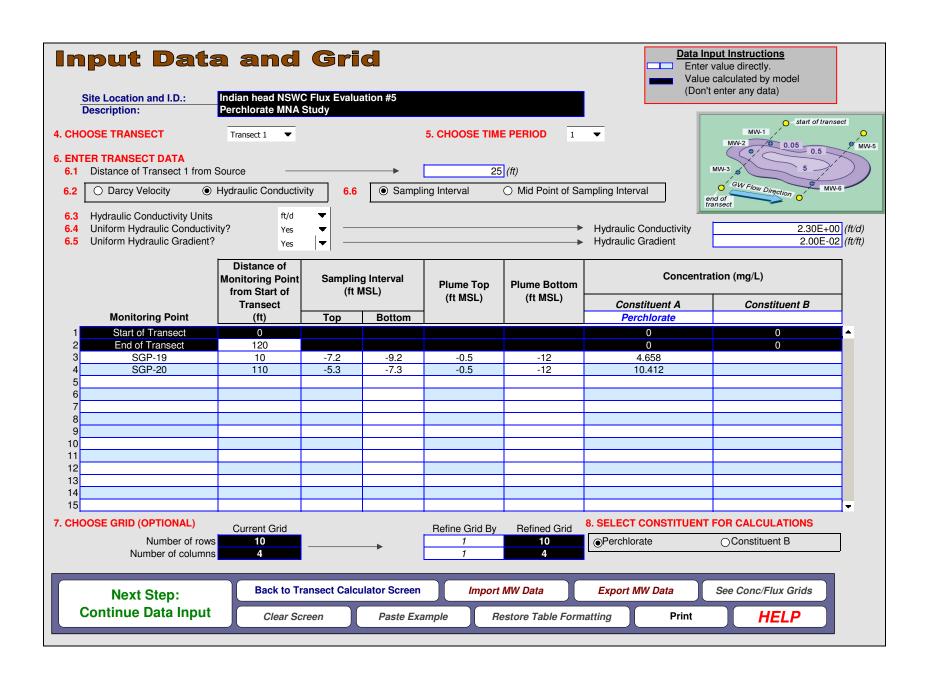
Appendix D

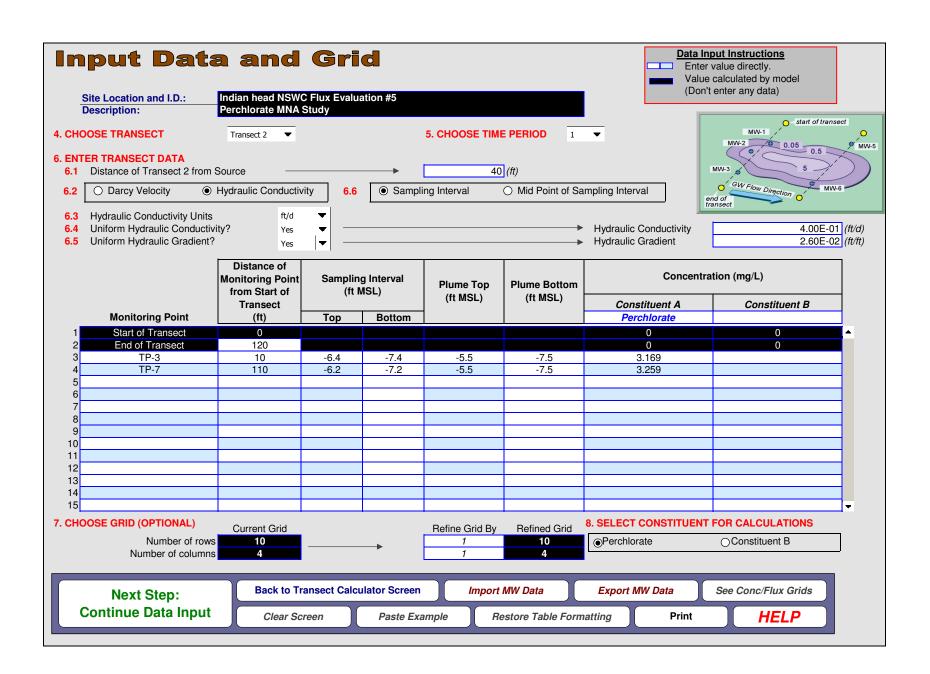
Natural Attenuation Rate Calculations

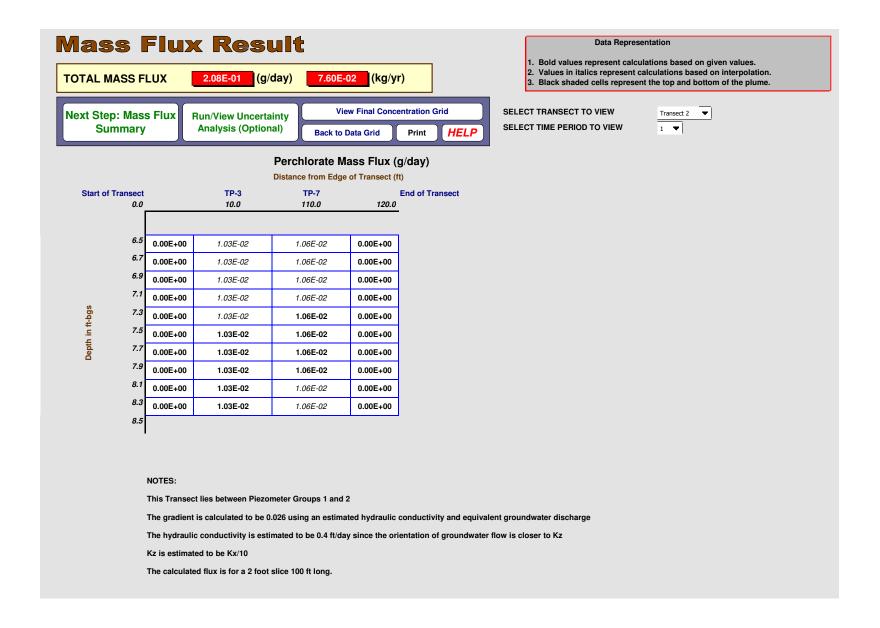
APPENDIX D											
APPENDIX D Attenuation Rates & Associated Statistics											
Monitoring Well	Estimated Ra	ate and Time Order)	Estimated Rate and Time (90%CI 1st order)		F Statistic (F<0.1)	Estimated Rate and Time (zero-order linear)			Estimated Rate and Time (90%CI Linear)		F Statistic (F<0.1)
	Rate (per day)	R squared	Rate	Time* (Years)		Rate (µg/L/day)	R squared	Time* (Years)	Rate	Time* (Years)	
Land Wells											
MW-1	-8.7E-04	0.63	-3.6E-04	67	0.06	-3.7E+01	0.60	7	-1.4E+01	25	0.06
MW-2	-3.5E-03	0.79			0.11	-1.2E+00	0.89	4	-6.5E-01	7	0.05
MW-3	7.2E-04	0.50	1.3E-03		0.12	3.1E+00	0.34		6.5E+00		0.22
MW-4	-1.4E-03	0.91	-1.1E-03	23	0.00	-8.0E+01	0.84	5.5	-5.3E+01	10	0.01
SGP-1S	7.5E-05	0.01	1.1E-03		0.90	3.8E-01	0.04		2.8E+00		0.90
SGP-1D	-5.7E-05	0.00	2.4E-03		0.97	6.5E-01	0.03		5.2E+00		0.81
SGP-2S	6.6E-04	0.30			0.45	-3.0E+00	0.26		3.6E+00		0.48
SGP-2D	-5.3E-04	0.06			0.69	-8.8E+00	0.07		2.1E+01		0.65
SGP-3S	-1.0E-03	0.42	5.6E-03		0.35	-2.0E-02	0.27		2.4E-02		0.48
SGP-3D	7.1E-04	0.19	2.7E-03		0.56	1.1E-01	0.35		3.2E-01		0.40
SGP-4S	-2.2E-03	0.90	5.3E-05		0.21	-3.3E-01	0.93		-5.3E-02		0.17
SGP-4D	-1.0E-03	0.87	2.1E-04		0.23	-4.0E+00	0.86		-8.8E-01		0.24
SGP-5S	-1.3E-03	0.19	7.2E-03		0.70	-1.8E-01	0.46		4.2E-01		0.53
SGP-5D	-5.8E-04	0.40	1.6E-03		0.56	-1.6E-01	0.29		6.2E-01		0.63
SGP-6S	-1.6E-03	0.99	-1.2E-03	14	0.04	-1.4E+01	0.93		-2.6E+00		0.16
SGP-6D	4.5E-03	0.90	9.2E-03			NO Slope					
SGP-7S	3.0E-03	0.95	5.1E-03		0.14	5.8E-01	0.89		1.2E+00		0.21
SGP-7D	2.4E-03	0.94	4.4E-03		0.16	4.0E-01	1.00	-1	4.6E-01	-1	0.03
SGP-8S	-8.3E-04	0.70	8.4E-04		0.37	-1.6E+01	0.67		1.9E+01		0.39
SGP-8D	4.5E-03	0.90	9.2E-03		0.20	-1.8E-01	0.90		4.2E-01		0.20
TP-5	-6.6E-04	0.49	1.4E-03		0.50	-1.0E+00	0.51		2.1E+00		0.49
Littoral Zone											
SGP-9	-2.1E-03	0.07	0.00805		0.73	-9.0E-02	0.10		2.7E-01		0.68
SGP-19	1.0E-04	0.05	0.00051		0.71	4.5E-01	0.07		2.0E+00		0.68
SGP-20	-1.1E-03	0.11	0.00178		0.58	-6.8E+00	0.17		7.2E+00		0.48
SGP-21	NO DETEC	TIONS				NO DETECT:	IONS				
TP-1	3.9E-03	0.88	0.00817		0.22	8.4E-03	0.88		1.8E-02		0.22
TP-2	-4.0E-03	0.58	0.00639		0.44	-1.1E-02	0.58		1.8E-02		0.44
TP-3	5.0E-04	0.51	0.00199		0.49	1.5E+00	0.55		5.4E+00		0.46
TP-4	-4.3E-03	0.58	0.00689		0.44	-1.3E-02	0.58		2.1E-02		0.44
TP-6	-2.8E-03	0.58			0.45	-5.4E-03	0.58		8.7E-03		0.44
TP-7	9.0E-04	0.03	0.01543		0.88	1.5E+00	0.04		2.5E+01		0.87
Subtidal Channe	el										
SGP-22S	A D AAG										
SGP-22D	NO DETEC					NO DETECT					
SGP-22SW	7.1E-03		0.01274		0.15	1.0E-01			2.9E-01		0.34
SGP-23S	NO DETEC					NO DETECT					
SGP-23D	NO DETEC					NO DETECT					
SGP-23SW	NO DETEC					NO DETECT					
SGP-24S	NO DETEC					NO DETECT					
SGP-24D	NO DETEC					NO DETECT					
SGP-24SW	NO DETEC					NO DETECT					
001 -710 M	NO DETEC	110110				HODELECT	10110				

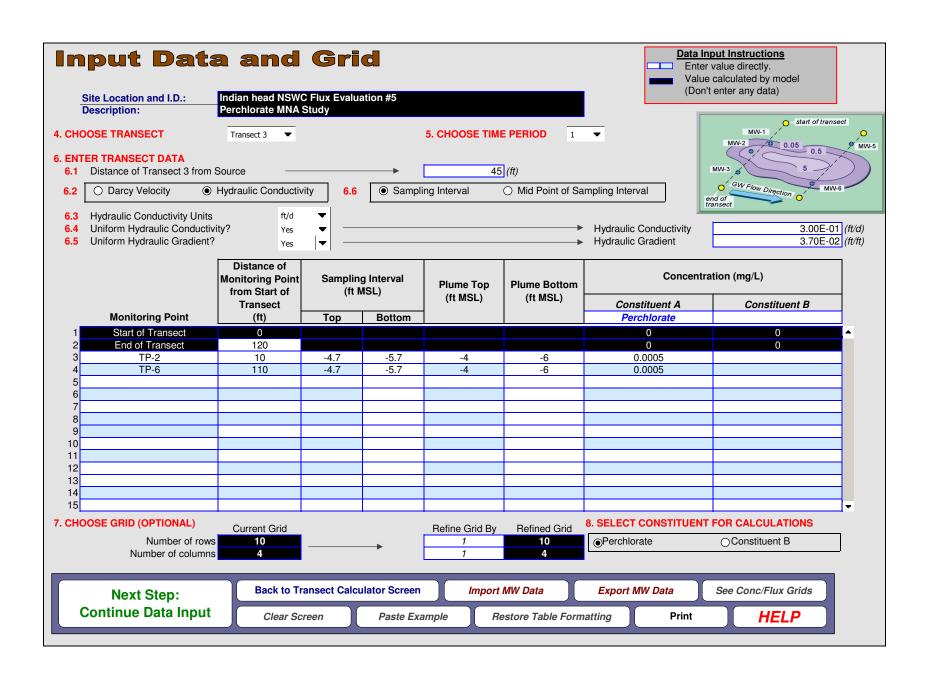
Appendix E

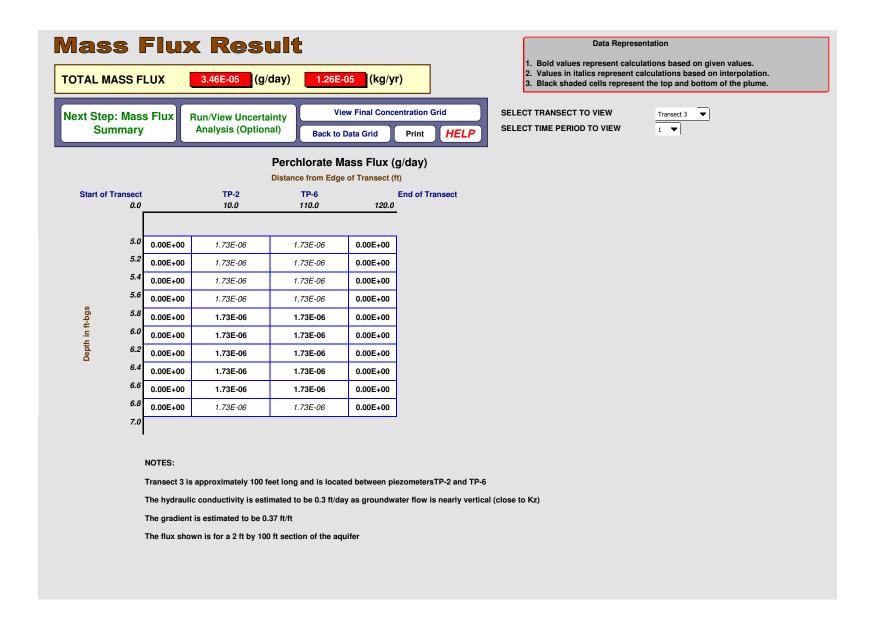
Mass Flux Calculations

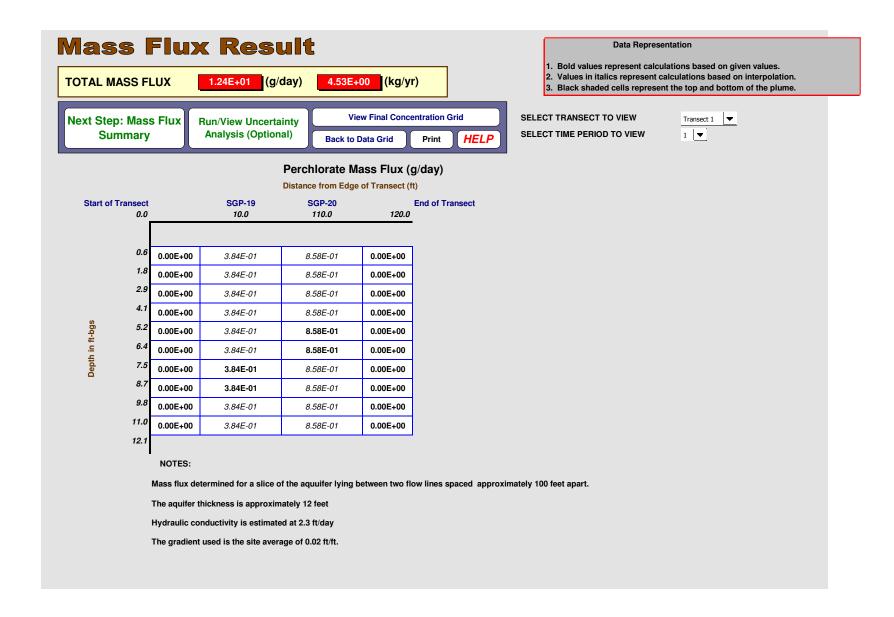












Appendix F

Macrocosm Study Results

	Appendix F Macrocosm Study Data								
Macrocosm ID	Day	Perchlorate (mg/L)	Chlorate (mg/L)	Chlorite (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Sulfate (mg/L)	
SGP-2D	0	4.3	<0.5	< 0.5	6.9	3.8	< 0.5	130	
#1	0	3.9	<0.5	<0.5	8.7	3.8	< 0.5	123	
	5	3.4	< 0.5	< 0.5	9.0	< 0.5	< 0.5	117	
	7	2.3	< 0.5	< 0.5	12	0.6	< 0.5	106	
#2	0	3.9	<0.5	<0.5	8.9	3.9	<0.5	123	
	5	3.8	<0.5	<0.5	8.8	1.4	<0.5	117	
	12	2.3	<0.5	<0.5	12	1.0	<0.5	108	
	19	1.3	<0.5	< 0.5	NS	NS	< 0.5	NS	
	20	0.2	< 0.5	< 0.5	NS	NS	< 0.5	NS	
#3	0	3.8	<0.5	<0.5	9.3	3.7	<0.5	121	
	5	3.3	< 0.5	< 0.5	9.0	1.7	< 0.5	112	
	12	<0.5	< 0.5	< 0.5	12	< 0.5	< 0.5	109	
	13	0.1	< 0.5	< 0.5	NS	NS	< 0.5	NS	
#4	0	3.7	<0.5	<0.5	9.5	3.7	<0.5	120	
	5	3.3	<0.5	<0.5	9.3	1.6	<0.5	114	
	12	2.0	<0.5	<0.5	12	0.9	<0.5	107	
	19	1.3	<0.5	< 0.5	NS	NS	< 0.5	NS	
	22	0.2	< 0.5	< 0.5	NS	NS	< 0.5	NS	
#5	0	3.8	<0.5	<0.5	9.4	3.8	<0.5	121	
-	5	3.4	<0.5	<0.5	9.3	0.8	<0.5	115	
	12	2.3	<0.5	<0.5	12	1.1	<0.5	107	
	19	1.5	<0.5	<0.5	NS	NS	< 0.5	NS	
	22	0.3	< 0.5	< 0.5	NS	NS	< 0.5	NS	

¹⁾ Analysis performed at the Laboratory of Environmental Engineering in the Department of Civil, Construction and Environmental Engineering at North Carolina State University, Raleigh, NC.
2) Incubations and analyses performed between March 28, 2007 (Day 0) and April 19, 2007 (Day 22)

Appendix G

Points of Contact

Appendix G Points of Contact

	Organization		
Point Of Contact Name	Name and Address	Phone/Fax/email	Role in Project
Dr. Robert C. Borden, P.E.	Solutions-IES	919-873-1060	Principal Investigator
	1101 Nowell Road	919-873-1074 (fax)	
	Raleigh, NC 276159	rcborden@eos.ncsu.edu	
M. Tony Lieberman, R.S.M.	Solutions-IES	919-873-1060	Co-Principal
	1101 Nowell Road	919-873-1074 (fax)	Investigator; Project
	Raleigh, NC 276159	tlieberman@solutions-ies.com	Manager
Mark B. Yeaton.	Naval Support Facility, Indian Head	(301) 744-2272	Indian Head Site Contact
	Environmental Program Office	mark.b.yeaton@navy.mil	
	3942 Ward Road, Suite 101		
	Indian Head, MD 20640-5157		